

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant:	Bruce E. Kreischer	§	
		§	Group Art Unit: 1797
Serial No.:	10/792,108	§	
		§	Examiner: Randy Boyer
Filed:	March 3, 2004	§	
		§	Confirmation No.: 4102
For:	A METHOD AND SYSTEM FOR SEPARATING AN OLIGOMERIZATION REACTOR EFFLUENT	§	

CERTIFICATE OF EFS-WEB FILING

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REPLY BRIEF

Dear Sir:

This Reply Brief is filed in support of the *Notice of Appeal* filed September 25, 2007 and the *Appeal Brief* filed November 26, 2007, and in response to the *Examiner's Answer* filed December 26, 2007. The Applicant authorizes all required fees under 37 C.F.R. § 1.17 to be charged to Deposit Account No. 50-1515, of Conley Rose, P.C. of Texas.

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I. STATUS OF THE CLAIMS

A. Total Number of Claims in the Application

Claims in the application: 1-35.

B. Status of All Claims in the Application

1. Claims canceled: 17-19, 27, and 35.
2. Claims withdrawn from consideration but not canceled: None.
3. Claims pending: 1-16, 20-26, and 28-34.
4. Claims allowed: None.
5. Claims rejected: 1-16, 20-26, and 28-34.
6. Claims neither rejected nor allowed: None.

C. Claims on Appeal

Claims on appeal: 1-16, 20-26, and 28-34.

II. GROUND FOR REJECTION TO BE REVIEWED ON APPEAL

The Examiner's notation of the grounds of rejection is correct. *See Examiner's Answer*, p.

2-3. Thus, the grounds of rejection to be reviewed on appeal are:

1. Whether claims 1-8, 14-16, 20-26, and 28-34 are unpatentable over WO 03/053890 (*Dixon*) in view of *Seader*, et al., Perry's Chemical Engineers' Handbook, 7th Ed., New York, McGraw Hill, 1997, pp. 13-4 – 13-9 (*Seader*) under 35 U.S.C. § 103(a).
2. Whether claims 1-13 are unpatentable over WO 99/19280 (*Woodard*) in view of *Seader* under 35 U.S.C. § 103(a).

III. ARGUMENT

A. **To the extent that the Examiner's Answer contains new rejections, the Applicants elect to continue the appeal.**

The Examiner's Answer appears to contain arguments and/or positions that were not presented prior to the Notice of Appeal. To the extent that these arguments and/or positions represent new grounds of rejection or new arguments under 37 C.F.R. § 41.39(a)(2), the Applicants elect to continue the Appeal of the present application under 37 C.F.R. § 41.39(b)(2), and address the new arguments and/or positions below.

B. **Prefractionation is not a means for flashing.**

In the Examiner's Answer, the Examiner states that his position is that the processes of *Dixon* or *Woodard* can be modified by either (1) perform the claimed separation by using the setup of *Seader's* Fig. 13-6(b) as it is shown in that figure with the first column (which *Seader* refers to as the "prefractionator") serving as a means for "flashing the oligomerization reactor effluent into a liquid portion and a vapor portion," or (2) performing the claimed separation by replacing the Petlyuk Towers' prefractionator with the flash drum of *Seader's* Fig. 13-7(a) and whereby the flash drum would deliver separate vapor and liquid input streams to the second column of *Seader's* Fig. 13-6(b). See Examiner's Answer, p. 13. The Examiner further asserts that the Applicants' Appeal Brief ignores his first position and only addresses his second position. *Id.* In response, the Applicants assert that the arguments provided in the Appeal Brief are equally applicable to either of the Examiner's positions. However, in an effort to clarify the Applicants' position, the Applicants specifically address each of the Examiner's positions below.

In the Examiner's Answer, the Examiner asserts that the Petlyuk Towers' prefractionator can be a means for the claimed flashing. *Id.* at pp. 14-15. Such a position is only possible via the *ex post* reasoning and hindsight bias described by the KSR court. See *KSR Int'l Co. v. Teleflex Inc.*,

550 U.S. ___, 82 USPQ2d 1385, 1397 (2007). Regardless, the Petlyuk Towers' prefractionation taught by *Seader* is not the same as the flashing recited in the claims. Indeed, there are numerous differences between flashing and Petlyuk Towers' prefractionation. First, flashing is a single-stage process. In contrast, the Petlyuk Towers' prefractionator is a multistage process¹. Thus, *Seader's* disclosure of multi-stage prefractionation cannot be a means for single-stage flashing. Second, flashing as a single-stage process does not need a condenser and reboiler or any means that function as a condenser and reboiler. In contrast, the Petlyuk Towers' prefractionator is a distillation column wherein the condenser and reboiler function is accomplished by returning a liquid stream and a vapor stream, respectively, from the Petlyuk Towers' second distillation column (the fractionator) to the Petlyuk Towers' prefractionator. As described herein, the Petlyuk Towers' prefractionator must receive the liquid stream and a vapor stream from the fractionator to obtain the benefits of the Petlyuk Towers described within *Seader*. Moreover, *Seader* teaches away from the interchangeability of prefractionation and flashing, as explained below.

C. *Seader* teaches away from the interchangeability of flash drums and Petlyuk Towers.

The Examiner contends that a prior art reference teaches away from a proposed modification only when the proposed modification would render the base reference inoperable for its intended purpose, and cites *McGinley v. Franklin Sports, Inc.*, 60 USPQ2d 1001 (Fed. Cir. 2001) in support. See *Examiner's Answer*, p. 17. However, the situations in which a prior art reference may teach away from a proposed modification are not as limited as the Examiner would lead us to believe. Rather, the Supreme Court and the Court of Appeals for the Federal Circuit (CAFC) have observed that "[e]vidence rebutting a *prima facie* case of obviousness can include ...

¹ *Seader's* Fig. 13-6(b) indicates that the prefractionator has N stages. N is understood to be at least two.

evidence that the prior art teaches away from the claimed invention in any material respect.” *In re Sullivan*, 84 USPQ2d 1034, 1038 (Fed. Cir. 2007) (emphasis ours). Examples of situations where the courts have found that the prior art teaches away from a proposed modification include:

- When the prior art expressly excludes an element of the proposed modification. *See In re Grasselli*, 218 USPQ 769 (Fed. Cir. 1983).
- When the prior art warns of the risks involved in making the proposed modification. *See United States v. Adams*, 383 U.S. 39, 148 USPQ 479 (1966).
- When the proposed modification would render the result inoperable for its intended purpose. *See In re Gordon*, 221 USPQ 1125 (Fed. Cir. 1984).
- When the proposed modification would render the result inoperable. *See McGinley v. Franklin Sports, Inc.*, 60 USPQ2d 1001 (Fed. Cir. 2001).
- When the prior art criticizes, discredits, or otherwise discourages the proposed modification. *See In re Fulton*, 73 USPQ2d 1141 (Fed. Cir. 2004).
- When a person of ordinary skill, upon reading the reference, would be discouraged from making the proposed modification or would be led in a direction divergent from the proposed modification. *See In re ICON Health & Fitness*, 83 USPQ2d 1746 (Fed. Cir. 2007).

Thus, when the prior art teaches away from the proposed modification in any material respect, such as in any of the above situations, the proposed modification cannot be used to render the claimed invention obvious.

In the instant case, *Seader* describes a plurality of different separation systems. Examples of such include single-stage separators such as flash drums, multi-stage separators such as

distillation towers, thermally coupled systems such as Petlyuk Towers, extractive distillation, azeotropic distillation, and batch distillation, among others. Most of these separation systems are designed for specific purposes, and are not interchangeable. As such, *Seader* provides guidance as to the specific circumstances when each separation system may be used. As part of his guidance, *Seader* teaches away from both the interpretation that the Petlyuk Towers' prefractionator flashes the feed stream and the interchangeability of the flash drum for the Petlyuk Towers' prefractionator in the *Examiner-Modified Petlyuk System*. Initially, *Seader* teaches that thermally coupled systems and single-stage vapor-liquid separation systems are alternatives of each other:

[C]onventional sequences like those of Fig. 13-4 may not always be the optimal choice, particularly when species of intermediate volatility are present in large amounts in the feed or need not be recovered at high purity. Of particular interest are thermally coupled systems. ... Sometimes **alternative** single- or multiple-stage vapor-liquid separation operations of the types shown in Fig. 13-7, may be more suitable than distillation for the specified task. *Seader*, pp. 13-5 – 13-6.

Seader also describes the circumstances under which each of these alternatives is suitable. With regards to flash drums, *Seader* states:

A single-stage flash, as shown in Fig. 13-7a, may be appropriate if (1) **the relative volatility between the two components to be separated is very large**; (2) the recovery of only one component, **without regard to the separation of the other components**, in one of the two product streams is to be achieved; or (3) **only a partial separation is to be made**. *Seader*, p. 13-6.

As described above, the flash drum is suitable for those situations where:

- the relative volatility between the lightest component and the heaviest component is very large;
- the vapor phase effluent comprises substantially all of the lightest component and some of the heaviest component, and the liquid phase effluent comprises substantially none of the lightest component and some of the heaviest component;
- the vapor phase effluent comprises some of the lightest component and substantially none of the heaviest component, and the liquid phase effluent comprises some of the lightest component and substantially all of the heaviest component; or
- only a partial separation of the lightest and heaviest components is desired.

With regards to Petlyuk Towers, *Seader* states:

Petlyuk towers [are] particularly useful for reducing energy requirements when the initial feed contains close-boiling species. Shown for a ternary feed, the first column in Fig. 13-6b is a prefractionator, which sends essentially all of the light component and heavy component to the distillate and bottoms respectively, but permits the component of intermediate volatility to be split between the distillate and bottoms. *Seader*, p. 13-5.

As described above, *Seader* teaches that the Petlyuk Towers are suitable for those instances where the relative volatility between components is small and wherein the Petlyuk Towers' prefractionator separates the lightest and heaviest components such that:

- the distillate comprises substantially all of the lightest component and substantially none of the heaviest component;
- the bottoms comprises substantially none of the lightest component and substantially all of the heaviest component; and
- the lightest and the heaviest components are substantially separated from each other.

As described above, the flash drum and Petlyuk Towers' prefractionator are mutually exclusive separation devices because they separate the lightest and heavy components to a different degree; that is, a partial separation versus a substantially complete separation, respectively. As such, *Seader* teaches away from the use of the prefractionator as a means for flashing and the interchangeability of the flash drum for the prefractionator. Specifically, since the Petlyuk Towers' prefractionator is used for substantially complete separation of the lightest and heaviest components, the partial separation of the lightest and heaviest components afforded by use of the flash drum (in place of the prefractionator) would change the distribution of not only the lightest and heaviest components but also the intermediate component in the distillate and bottoms fraction provided to the Petlyuk Towers' fractionator. Recovery of any intermediate components would be dependent on the volatility of the intermediate component relative to the lightest and heaviest components. Because the flash drum does not provide the same separation as the Petlyuk Towers' prefractionator, the flash drum would not be expected to provide the separation required to enable the fractionator to perform the desired separation of the intermediate component. Because *Seader* teaches that the Petlyuk Towers' prefractionator and the flash drum are mutually exclusive separation devices, *Seader* teaches away from both the interpretation that the prefractionator flashes the feed stream and the substitution of the prefractionator for the flash drum in the

Examiner-Modified Petlyuk System. Consequently, *Seader* cannot be combined with *Dixon* or *Woodard* to render obvious the pending claims.

Moreover, some references teach away from the use of Petlyuk Towers altogether. U.S. Patent 6,347,533 (*Tung*) contains a thorough description of the rigorous design and operating constraints associated with the Petlyuk Towers. See *Tung*, col. 1, line 19 – col. 3, line 34. *Tung* also observes that the Petlyuk Tower design has never been successfully operated in a commercial environment. See *Tung*, col. 1, lines 52-53. Thus, *Tung* teaches away from the use of the Petlyuk Towers. Moreover, *Tung* represents evidence of the failure of others to implement the Petlyuk Towers, and as such is further evidence of non-obviousness.

D. Removing or minimizing the reflux in the prefractionator changes the principle of operation of the Petlyuk Towers.

The Examiner also contends that the elimination of the reflux from the prefractionator would not destroy the principle of operation of the Petlyuk Towers, and that such would be no worse than a very small reflux ratio. See *Examiner's Answer*, pp. 15-16. Applicants specifically point out that by definition, the Petlyuk Towers' prefractionator must have some measureable reflux and by having any measurable reflux ratio, the Petlyuk Towers' prefractionator would not represent a means for flashing. Additionally, the Applicants question whether the Examiner's proposed very small reflux ratio is even possible. Specifically, some authors have commented on the rigorous design and operating constraints of the Petlyuk Towers and indicate that, at least in some embodiments, operable solutions for the Petlyuk Towers are not possible below certain reflux ratios. See Chavez et al., *Multiple Steady-State Solutions for Interlinked Separation Systems*, Ind. Eng. Chem. Fundam. 25:566-576, 569 (1986). Thus, a detailed analysis (or experimentation) would have to be performed to determine what the exact minimum reflux ratio for Petlyuk Towers is in any given specific implementation, e.g. the process of *Dixon* or *Woodard*.

Specifically, it is possible that the Petlyuk Towers are not operable at a minimal reflux ratio when implemented with the processes of *Dixon* or *Woodard*, e.g. that a substantially higher minimum reflux ratio must be maintained to make the process operate. However, such cannot be determined without performing a detailed analysis of the process. In view of Chavez, the suggestion that the process of *Dixon* or *Woodard* could use Petlyuk Towers with a minimal prefractionator reflux ratio without a detailed analysis (or experimentation) hints at hindsight reconstruction.

Regardless, the Examiner's reasoning is strikingly similar to the line of reasoning described in *In re Gordon*, 221 USPQ 1125. Mr. Gordon invented a blood filter assembly used during surgery and other medical procedures involving the handling of blood to remove clots, bone debris, tissue, or other foreign materials from blood before it is returned to a patient's body. Unlike other blood filter assemblies, his device permitted both entry of the blood into and discharge of the blood from the bottom end of the filter assembly. The Examiner rejected the claims as obvious in view of U.S. Patent 1,175,948 (*French*). *French* disclosed a liquid strainer for removing dirt and water from gasoline and other light oils, but *French's* device had both the inlet and outlet at the top end of his device. The Board of Appeals and Patent Interferences (the Board) affirmed the Examiner's rejection, reasoning that it would have been obvious to turn *French's* device upside-down to have both the inlet and outlet at the bottom, rather than at the top. In the Board's opinion, no patentable distinction was created by viewing *French's* device from one direction and the claimed apparatus from another. The CAFC reversed the Board's decision, stating:

The question is not whether a patentable distinction is created by viewing a prior art apparatus from one direction and a claimed apparatus from another, but, rather, whether it would have been obvious from a fair reading of the prior art reference as a whole to turn the prior art apparatus upside down. French teaches a liquid strainer which relies, at least in part, upon the assistance of gravity to separate undesired dirt and water from gasoline and other light oils. Therefore, it is not seen that French would have provided any motivation to one of ordinary skill in the art to employ the French apparatus in an upside down orientation. ...

Indeed, if the French apparatus were turned upside down, it would be rendered inoperable for its intended purpose. The gasoline to be filtered would be trapped in pocket, and the water French seeks to separate would flow freely out of the outlet. Further, unwanted dirt would build up in the space between the wall of shell and screen, so that, in time, screen would become clogged unless a drain valve, such as pet-cock, were re-introduced at the new “bottom” of the apparatus. In effect, French teaches away from the board’s proposed modification. 221 USPQ at 1127 (citations and reference number omitted).

As shown above, the CAFC held that where the proposed modification of the prior art renders the prior art invention inoperable for its intended purpose, the prior art teaches away from the proposed modification and does not render the claimed invention obvious.

Similar to the facts in *Gordon*, the Examiner’s proposed modification, either via a very small reflux ratio or via the *Examiner-Modified Petlyuk System*, renders the Petlyuk Towers inoperable for their intended purpose. Specifically, *Seader* teaches that Petlyuk Towers are a thermally coupled system in that the prefractionator obtains its reflux and boil-up from the fractionator instead of from a condenser and a reboiler:

Of particular interest are thermally coupled systems. ... The thermally coupled system in Fig. 13-6b, discussed by Stupin and Lockhart [citation omitted] and referred to as Petlyuk towers, is particularly useful for reducing energy requirements when the initial feed contains close-boiling species. ... Products from the prefractionator are sent to appropriate feed trays in the second column, where all three products are produced, the middle product being taken off as a sidestream. Only the second column is provided with [a] condenser and reboiler; reflux and boil-up for the prefractionator are obtained from the second column. *Seader*, p. 13-5.

As described above, the intended purpose of the Petlyuk Towers is to reduce the energy requirements of the process. The low energy consumption is obtained by thermally coupling the prefractionator to the fractionator using the vapor and liquid streams from the fractionator. Indeed, *Tung* observes that the thermal coupling is the *very reason* for selecting the Petlyuk Towers, since it is the thermal coupling that allows the Petlyuk Towers to be the “benchmark in lowest energy consumption.” *See Tung*, col. 1, lines 33-34. Thus, like the Examiner’s rejection in

Gordon, the Examiner's proposed modification of the prior art appears relatively simple, but modifies a critical element of the prior art that makes it useful for its intended purpose. Specifically, **if the liquid and vapor streams are minimized or completely removed from the Petlyuk Towers, then there is no thermal coupling between the Petlyuk Towers, and the Petlyuk Towers do not achieve their intended purpose of low energy consumption.** Moreover, minimizing or completely removing the vapor or liquid streams would ignore the plain meaning of the term used by *Seader* to describe the Petlyuk Towers: **Thermally-Coupled Systems**. Thus, the elimination of the thermal coupling changes the principle of operation of the Petlyuk Towers and renders them inoperable for their intended purpose. As such, both the Petlyuk Towers configured with a very small reflux ratio and the *Examiner-Modified Petlyuk System* are prohibited modifications of *Seader*, and cannot be used to with *Dixon* or *Woodard* to render obvious the pending claims.

IV. CONCLUSION

In view of the above arguments, the Applicant respectfully requests that the final rejection of the claims be reversed and the case advanced to issue. Should the Examiner feel that a telephone interview would advance prosecution of the instant application, Applicant invites the Examiner to call the attorneys of record.

The Commissioner is hereby authorized to charge payment of any further fees associated with any of the foregoing papers submitted herewith, or to credit any overpayment thereof, to Deposit Account No. 50-1515, of Conley Rose, P.C. of Texas.

Respectfully submitted,
CONLEY ROSE, P.C.

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V. **EVIDENCE APPENDIX**

The following evidence is submitted in support of the Appeal and to rebut positions taken by the Examiner:

1. U.S. Patent 6,347,533
2. Chavez et al., *Multiple Steady-State Solutions for Interlinked Separation Systems*, Ind. Eng. Chem. Fundam. 25:566-576 (1986).

(12) **United States Patent**
Tung

(10) **Patent No.:** **US 6,347,533 B1**
(45) **Date of Patent:** **Feb. 19, 2002**

(54) **HYDRAULICALLY BALANCED FULLY THERMALLY COUPLED SYSTEM**

(76) **Inventor:** **Peter Tung**, 63 Templer Dr., Ancaster (CA), L96 3X7

(*) **Notice:** Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) **Appl. No.:** **09/518,530**

(22) **Filed:** **Mar. 4, 2000**

(51) **Int. Cl. 7** **F25J 3/00; F25J 5/00**

(52) **U.S. Cl.** **62/620; 62/643; 62/631; 62/905**

(58) **Field of Search** **62/617, 643, 630, 62/905, 631, 620**

(56) **References Cited**

U.S. PATENT DOCUMENTS

1,549,236 A * 8/1925 Van Nuyss 62/617

1,782,287 A * 11/1930 Claude 62/643
1,885,059 A * 10/1932 Cicali 62/617
5,339,648 A * 8/1994 Lockett et al. 62/646
5,970,742 A * 10/1999 Agrawal et al. 62/630
6,106,674 A * 8/2000 Agrawal et al. 203/75

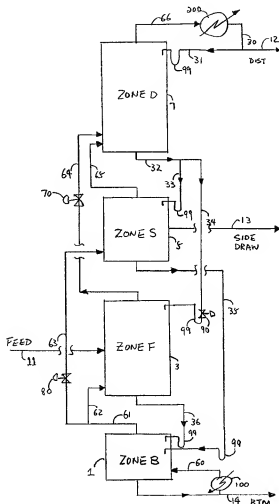
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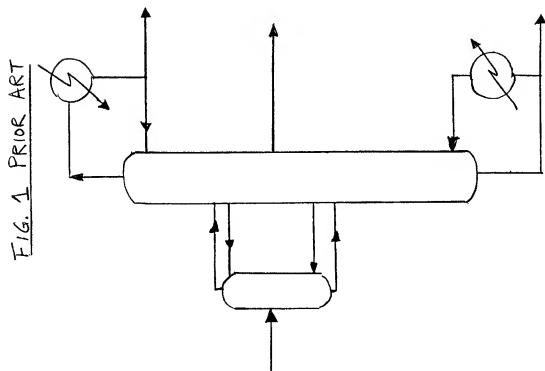
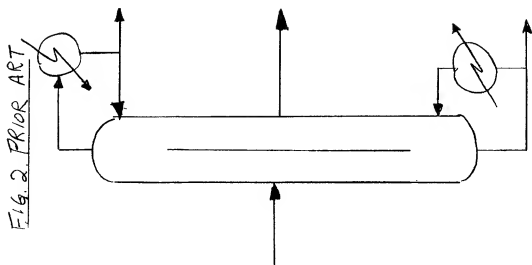
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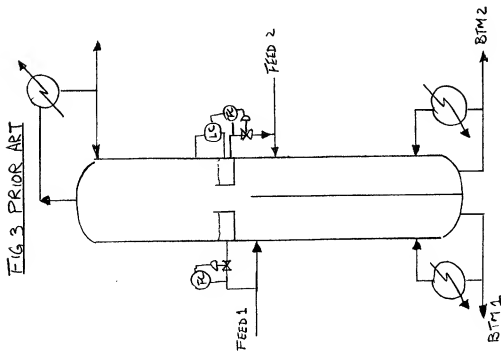
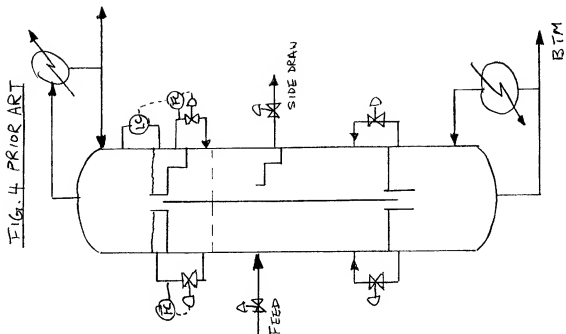
(57) **ABSTRACT**

A fully thermally coupled distillation structure designed to overcome hydraulic limitations in the past has been revealed for separating a multi-component feed stream into three product streams. The fractionation apparatus is equipped with at least one condenser and one reboiler to provide fractionation efficiency surpassing the PETLYUK system. Further, the fractionation apparatus includes innovative designs to enable hydraulically balanced and energy efficient operation at various feed rates, compositions and product specifications.

20 Claims, 7 Drawing Sheets







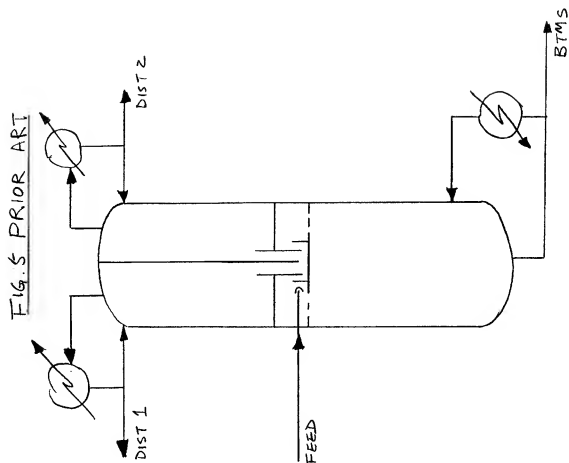


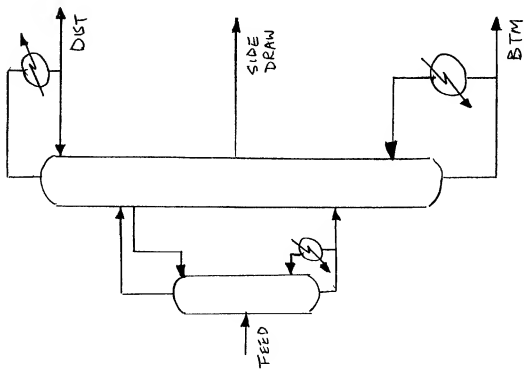
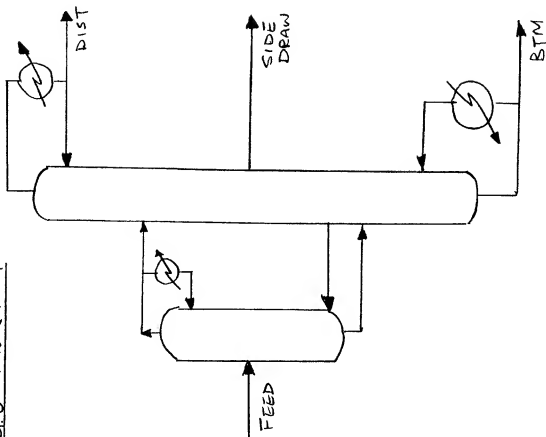
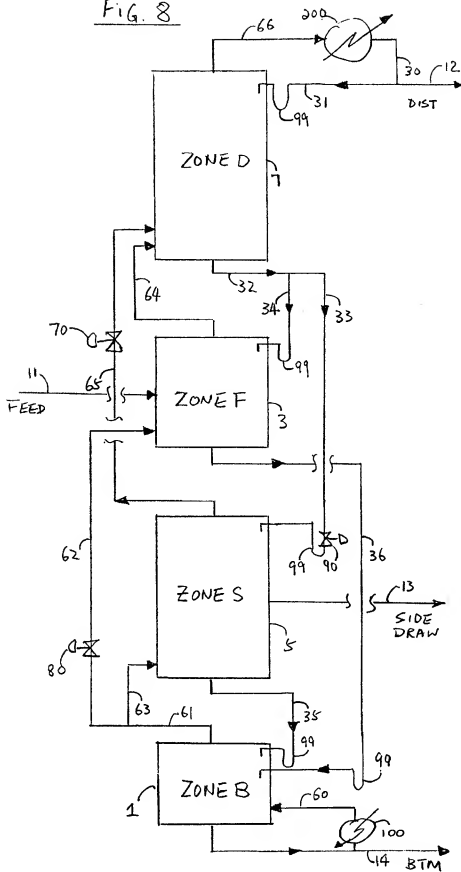
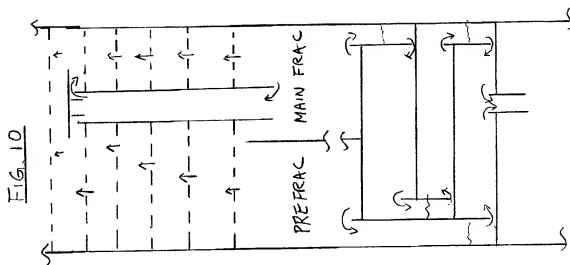
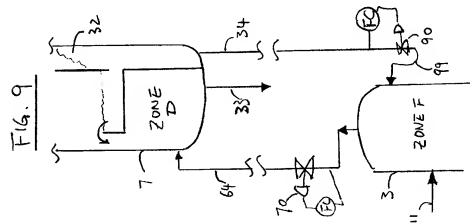
FIG. 6 PRIOR ART

FIG. 8





HYDRAULICALLY BALANCED FULLY THERMALLY COUPLED SYSTEM

BACKGROUND—FIELD OF THE INVENTION

This invention relates to a fractionation column and method of operation thereof. In a specific respect, the invention relates to separating at least one feed stream containing at least two components, into at least one overhead distillate stream, at least one side draw stream and at least one bottom stream, each such product stream containing different averaged volatility than the other product streams. The fractionation column is equipped with at least one condenser and at least one reboiler. Further, the fractionation apparatus includes innovative designs to enable hydraulically balanced and energy efficient operation at various feed rates, compositions and product specifications.

BACKGROUND—DISCUSSION OF PRIOR ART

In fractionation, it is sometimes desirable to separate a multi-component feed stream into a number of streams containing various fractions of desirable components in the product streams. For the case of one feed stream and two product streams, the separation can be accomplished by distillate and bottoms product draw. Further separation can be accomplished by repeating the two-product stream process to either the distillate or the bottoms streams. However, the introduction of additional columns will require a corresponding number of reboilers and condensers. That requirement, in turn, requires additional operating costs as the condensing and the reboiling process is being repeated. Numerous references can be found in prior art documenting efforts to lower both capital and operating costs in the above-mentioned separation. The benchmark of the lowest energy consumption has been set by the well-known PET-LYUK system as shown in FIG. 1.

In this configuration, a prefractionation column separates the feed into two streams using a split vapor stream from the main column's stripping section and a split liquid stream from the main column's rectifying section. The resulting vapor and liquid streams exiting from the prefractionation column are richer in light and heavy components respectively. These two semi-processed streams are then fed back to the main column. This configuration provides an advantage allowing the main fractionation column to enhance the purity of the side stream draw. In turn, the main fractionation column also provides the stripping section and the rectifying section with better quality feeds. The combined effect is a very efficient use of vapor/liquid traffic to yield three product streams. The drawback from such an ingenious design is that the vapor and liquid streams at the communicating cross-overs are almost at the same operating pressures, making the column next to impossible to operate. Consequently, not one such design has ever been operated commercially.

Wright in U.S. Pat. No. 2,471,134 proposed to combine the prefractionation and main columns into one fractionation unit by erecting a partition along the center part of a column. The column is equipped with one overhead condenser and one bottom reboiler. This prior art is shown in FIG. 2. This setup is effective in overcoming the hydraulic limitations in the PETLYUK system. At the same time, it reduces capital costs by having only one common shell. However, the fixed internals offers no adjustments in vapor/liquid traffic in either side of the partition. As feed quality and rate changes, the desired operating range could very easily fall outside of the original design envelope.

In U.S. Pat. No. 3,053,521 Plaster and Dixon taught the use of introducing a tray in a column having a large cross

sectional area. The level of the stored liquid in the tray affects the rate of internal liquid flow through a perforated weir. Resetting a side draw flow controller controls the level in the tray. That effectively controls the internal liquid traffic in the column.

Graven taught the use of a partitioned stripping section as shown in FIG. 3 using two reboilers on either side of the partition in U.S. Pat. No. 3,412,016. This configuration handles two feeds with different quality of higher boiler contents and economizes by sharing a common rectifying section. Two bottoms product streams and one distillate product stream result from such a configuration.

In U.S. Pat. No. 4,230,533, as shown in FIG. 4, Giroux taught the use of a method to adjust vapor and liquid traffic in a divided wall column that was described by Wright earlier. The proposed column internals and additional control loops were designed to provide control of liquid and vapor traffic in the two sides of the internal partition. Unlike Wright's design, which has fixed internal arrangement, Giroux's proposal claimed to be able to handle changes in feed rate, quality and product specifications. The very concept of a divided wall column configuration has one obvious intrinsic limitation. By sharing a partition, the stages available for prefractionation and main fractionation is tied. In other words, the ratio of stages between feed side and product side cannot deviate too far away from unity. Some design scenarios, however, may be more effective if that ratio is allowed to be higher or lower than unity.

Two other U.S. Patents also made reference to the PET-LYUK benchmark. They are described as follows:

U.S. Pat. No. 5,755,933 assigned to M.W. Kellogg Company of Houston Tex. taught the use of a partitioned rectification section, each having its condenser in the overhead as shown in FIG. 5. The lightest product stream is to be collected as distillate on the feed side of the partition. The intermediate product stream is to be collected as the distillate from the other overhead condenser. The heaviest product is to be recovered as the bottoms. This design offers a unique benefit as the vapor flow is directly affected by the corresponding condenser duty. Increasing the condensing duty in either one of the overhead condensers causes a local vapor inventory decrease as vapor is condensed to form liquid. The corresponding lower pressure at the top will cause higher flow of vapor flowing upwards. As well, the reflux can be increased to effect higher liquid/vapor traffic. However, there are a few drawbacks in this proposed configuration.

1) A vaporized feed is highly recommended in order to prevent the light products from passing under the partition. Should that be allowed to happen, the intermediate component will be irreversibly contaminated with the light products.

2) The partition gives the two rectifying sections roughly the same number of stages. That requirement, again, may not be the most desirable design.

3) An additional condenser is required.

U.S. Pat. No. 5,970,742 assigned to Air Products and Chemicals Inc. of Allentown Penn. taught the use of a "modified" PETLYUK system. In this design, liquid and vapor is being generated in the prefractionation column by adding a condenser or a reboiler respectively as shown in FIG. 6. The Patent claims to be almost as energy efficient as the PETLYUK system. A simple analysis would arrive at quite a different conclusion. Let us consider the prefractionation condenser in this configuration. Since this secondary reflux is generated by the secondary condenser, which is

situated at a point below the main condenser, the secondary reflux is effectively bypassing the top section of the main column. Similarly, the reboiler duty used in the prefractionation column is again effectively bypassing the bottom stripping section of the main column. Therefore, thermodynamically, this configuration can never be as efficient as the PETLYUK system. The departure from the benchmark in the condenser configuration depends on the relative volatility between the lightest product and the intermediate product as well as the stages above the vapor return to the main column. In effect, how much fractionation the internal reflux bypassing is giving up. Similarly, the departure from the benchmark in the reboiler configuration depends on the relative volatility between the intermediate product and the heavy product and the stages below the liquid return to the main column. In effect, how much fractionation the vapor bypassing is giving up. Obviously, an additional heat exchanger is required in this configuration. Not so obvious is the hydraulic difficulty in the condenser scenario. Unlike the Kellogg arrangement where the condenser can vary its duties at will and create vapor traffic as a result of condensing vapor, this prior art faces competing vapors from both columns. This poses further operating difficulty in varying the secondary condenser duty.

As can be seen from the prior art cited above, a truly fully thermally coupled column has yet to be reduced to practice. Another area of improvement needs to be addressed from a thermodynamic efficiency perspective. In the shared rectification section of the two columns, the vapor streams from the two columns could contain very different qualities of vapor. The same reasoning applies to the liquids entering the shared stripping section. Should these streams be mixed?

A hydraulically balanced and thermodynamically efficient fully thermally coupled column has yet to emerge.

OBJECTS AND ADVANTAGES

Accordingly, several objects and advantages of this invention are:

The present invention focuses on overcoming the difficulties in making a fully thermally coupled column hydraulically operable and capturing the thermodynamic efficiency that such system could provide.

The present invention takes the approach of built-in design flexibility so that the resulting apparatus and control method can cover a wide range of operating scenarios.

It is another object of this invention to challenge the benchmark set by the PETLYUK system and to find ways to achieve a even higher thermodynamic efficiency than was previously thought to be the practical limitation.

It is another object of this invention to further improve the efficiency of a divided wall column by further analysis of the mixing zones in the column.

It is yet another object of the invention to generalize the system for use in a two component system separation.

It is yet another objective of this invention to illustrate the method and opportunity of applying this invention to retrofitting existing columns.

It is yet another objective of this invention to enable reactive distillation to be carried out in a more confined process environment to further improve reaction selectivity.

Further objects and advantages of this invention will become apparent from a consideration of drawings and ensuing description.

DESCRIPTION OF THE DRAWINGS

FIG. 1 shows the well-known benchmark PETLYUK system.

FIG. 2 shows Wright's divided wall column.

FIG. 3 shows Graven's two reboilers and one condenser divided wall column.

FIG. 4 shows Giroux's divided wall column with vapor and liquid control loops.

FIG. 5 shows Kellogg's two condensers and one reboiler divided wall column.

FIG. 6 shows Air Product's modified PETLYUK column.

FIG. 7 shows a typical HBFTC system.

FIG. 8 shows one alternate arrangement of a HBFTC system.

FIG. 9 shows column internals for rationing internal liquid flow.

FIG. 10 shows column internals to improve divided wall column efficiencies.

SUMMARY

The summary of this invention is an apparatus and corresponding control method to separate a feed stream containing at least two different boiling point components into three product streams. The apparatus used is hydraulically balanced and fully thermally coupled. The apparatus comprised of one common stripping section, one prefractionation section, one main fractionation section and one common rectification section. The column is equipped with at least one reboiler and at least one condenser. All sections can be designed to have different number of stages while preferably sharing the same diameter, though not a requirement. The internal and external connections, control valves and special arrangements are designed to provide the controllability of the column over a wide range of operating conditions. This invention matches, or even surpasses, the level of energy efficiency as benchmarked by the PETLYUK system.

DESCRIPTION OF THE INVENTION

This invention relates to a separation apparatus that takes a multi-component feed stream containing at least two key components targeted for separation. The feed stream is fractionated into three product streams, each containing different fractions of components resulting in different average boiling points or averaged volatility. It is to be understood that the scope of the present invention is not to be limited by the following examples. They are merely for further clarification purpose.

One petrochemical example is to separate a 60/40 mixture of ethylene and ethane (only two components) stream into three product streams. One light stream has an ethylene specification of 99.5% purity, a typical polymer grade. The heavy stream has an ethane specification of say 95% for recycle to cracking heaters, and the intermediate dilute ethylene stream targeting for a 75% ethylene content for special polymerization reactions.

Another example in an oil refinery scenario could be to separate a hydrofined feed stock into three product streams with different boiling point ranges. The feed has a 5% boiling point of say 200 degrees F. and a 95% boiling point of 400 degrees F. and covers a wide spectrum of components.

The later example illustrates that the scheme shows the particular component, or components, which the respective product stream is enriched in, but does not necessarily mean the absence of other components in that product stream. This invention is tailored to perform the required separation with

efficient use of energy, ease of operation and low capital costs. Before describing the invention in detail, analysis of relevant prior art will aid in the understanding of the concepts of this invention.

Background

It is commonly accepted that the PETLYUK system is the most efficient system in separating a feed stream into three product streams. The reason behind this high efficiency is the fully thermally coupled configuration. This configuration allows efficient use of vapor, generated from the only reboiler, and liquid, generated from the only condenser, to run the full course of the stages provided for vapor/liquid contact. Therefore, for a given number of stages, feed composition, product specification and operating pressure, the PETLYUK system requires the least amount of reboiler duty.

A close match is Wright's proposal, using a divided wall column to mechanically preset the vapor/liquid splits in the parallel system. This setup inevitably surrenders the flexibility of making adjustments to handle future feed quality, rate and product specification changes. In other words, Wright's system could achieve the PETLYUK efficiency for a particular feed condition if designed properly, but may not be possible at other operating conditions. The rate of heat transfer across the partition adds to the confusion as well.

In U.S. Pat No. 4,230,533, Giroux recognized the above built-in limitation on operational flexibility and proposed an internal liquid/vapor control mechanism for a divided wall column. It is an admirable attempt using state of the art control techniques at the time. However, the operating range and stability is still quite limited. It is of high relevance to analyze the cause of limitations before the full impact of the present invention can be appreciated.

For this reason, a detailed hydraulic analysis of Giroux's design is discussed below.

For the splitting of liquid flow without using a pump as proposed:

It is a major challenge to control the internal liquid split between the two partitioned sections using only hydrostatic head. Hydrostatic head available is the elevation between the liquid level at the reservoir above and the liquid level at the tray below. In theory, there is no limit on the available head. In practice, however, the non-productive column height could be filled with mass transfer media and better utilized to provide additional separation. Furthermore, flow varies with the square root of pressure difference. It would follow that for a given maximum available hydrostatic head, the control valve would soon be limited and cannot provide an effective control range.

Splitting vapor flow is even more challenging because excessive pressure drop would cause Downcomer backup unless very tall Downcomers are used.

To further illustrate this very important point, let us consider the vapor passage across a trayed column. The pressure drop across a tray, at a given vapor flow rate, is a function of the resistance across the active area on the tray. The column, for pressure drop consideration, is essentially a series of orifice plates. Some control application has inferred vapor flow across the column by the measured pressure drop across the column, square rooted. This reasoning is also applicable to other mass transfer apparatus such as packing. Again, the question is how much height in a column can be sacrificed in order to give a reasonable vapor flow control range.

Clearly, Giroux's proposal still cannot provide the much-needed operating flexibility that has been identified for quite some time. The present invention focuses on overcoming the

limitations in prior art and proposes a hydraulically balanced system. Before going into details of such a novel invention, another thermodynamic point may not have been previously explored due to the hydraulic balance hurdle. Thermodynamic analysis of the PETLYUK system particularly the vapor mixing and liquid mixing zones is as follows:

Let us focus on the vapor/liquid traffic at the top of the partition of a divided wall column, FIG. 2, (special application of the PETLYUK system) as an illustration. At the top end of the partition, the two streams of vapor from both sides of the partition emerge. The vapor from the prefractionation side, feed side, can be regarded as the primary feed to the rectifying section while the vapor from the main fractionation side, the side draw product side, as the secondary feed. The above is taken as a convention, with no reflection on stream quality. The quality of the respective streams depends on the degree of separation and the respective composition profile across the two columns. For instance, if the main column has a higher vapor liquid traffic than the prefractionation column to effect a finer separation, and the requirement of the intermediate product stream results in high light product content entering into the rectifying section, then the secondary vapor stream is already better rectified than the corresponding vapor from the other side of the partition. It would be thermodynamically unwise to mix dissimilar streams together. A more efficient way would be to return the better stream to a higher location in the rectifying section.

The same reasoning can be applied towards the two liquid streams returning to the shared stripping section. Again, depending on operating condition, one of the streams could very well be better enriched with the heavy component than the other stream. Proper placement of the streams would give even better thermodynamic efficiency than suggested by the PETLYUK system. Therefore, based on the above thermodynamic efficiency consideration, the opportunity to challenge the benchmarked PETLYUK system exists. This additional focus will be explained in further details.

Present Invention

Let us examine the configuration as in FIG. 7 for illustration purpose. This arrangement, defined as one expression of a Hydraulically Balanced Fully Thermally Coupled system (HBFTC system), is a column equipped with one reboiler 100 and one condenser 200. Further, the column is divided into four operating zones, in ascending elevation as follows:

A stripping zone, zone B, 1 the bottoms product zone.

A prefractionation zone, zone F, 3 the feed zone.

A main fractionation zone, zone S, 5 the side stream draw off zone.

A rectifying zone, zone D, 7 the distillate product zone. By interchanging the position of S 5 and F 3, an alternate arrangement is shown in FIG. 8. The following is stream descriptions of each zone, interestingly enough, applies to both FIG. 7 and FIG. 8:

Prefractionation Zone, Zone F 3

A feed stream 11 enters zone F 3 and is separated into two streams, one liquid stream 36 rich in the heavy component and a vapor stream 64 that is rich in the light component. The separation is effected by two streams, one liquid and one vapor. The liquid stream 34, containing both light and intermediate components, enters zone F 3 from the rectifying zone, zone D 7. Another stream 62, which is a vapor stream, enters zone F 3 from the stripping zone, zone B 1 contains both intermediate and heavy components.

Stripping Zone, Zone B 1

Liquid 36 from zone F 3 and liquid 35 from zone S 5, both containing intermediate and heavy components enters zone

B 1 at the upper section. Vapor 60 generated from the reboiler 100 in zone B 1 causes the separation of intermediate component from the heavy component. The resulting stripped liquid is routed away as the bottoms product stream 14. The vapor stream 61 leaving zone B 1, which contains intermediate and heavy components is split into two separate streams, one stream 62 is routed to the prefractionation zone, zone F 3 and the other stream 63 enters the main fractionation zone, zone S 5. The quantity of each vapor flow from zone B 1 is rationed. The method of rationing and the resulting effect will be discussed in further details later. Rectifying Zone, Zone D 7

Vapor 64 from zone F 3 and vapor 65 from zone S 5, both containing intermediate and heavy components enters zone D 7 at the lower section. Liquid 30 generated from the condenser 200 enters zone D 7 at the top, causes the separation of light component from the intermediate component. The resulting rectified vapor 66 is condensed 30 and routed away as the distillate product stream 12. The internal reflux 31 also generates a liquid stream. This liquid stream 32 leaving zone D 7, which contains light and intermediate components is split into two separate streams, one stream 33 is routed to the main fractionation zone, zone S 5 below and the other stream 34 enters zone F 3 below. Like the vapors 62 and 63 from zone B 1, the quantity of each liquid flow 33 and 34 from zone D 7 is also rationed. The method of rationing and the resulting effect will be discussed in further details later.

Main Fractionation Zone, Zone S 5

Vapor 63 from zone B 1 enters this zone, zone S 5 from the bottom. Liquid 33 from zone D 7 enters from the top. The resulting fractionation generates a vapor stream 65 and a liquid stream 35 plus a side draw 13 that contains the predominant intermediate component. The vapor stream 65 exits the top and enters zone D 7 at the lower section while the liquid 35 exits the bottom and enters zone B 1 at an upper section.

The above completes the routing of one HBTFC system.

One of the many special features in this invention is the unparalleled ability to hydraulically balance the vapor and liquid flows across all the zones and maintain operating flexibility. The following is a step by step analysis of all the communicated zones and the method of achieving hydraulic balance.

Hydraulic Analysis of Vapor Communication Loops as Shown in FIG. 7

Zone D 7 and zone S 5 can communicate freely and so can zone F 3 and zone B 1. The vapor lines between the two respective zones are acting like balance lines allowing liquid to flow down freely. Self-venting liquid lines can further eliminate the need for the vapor line piping requirement. Now let us focus on the overall vapor flow pattern across the column.

Vapor 61 exiting zone B 1 is to be split between two routes,

From B 1 via 63 through S 5 via 65 to D 7, the first path or

From B 1 via 62 through F 3 via 64 to D 7, the second path. Hydraulically, the relative resistances between the above two routes effect the actual vapor flow rates. If vapor-rationing target is to be maintained, relative resistances between the two parallel vapor paths have to be manipulated. That can be accomplished by adjusting the relative resistance by either:

Using manual valve 80 to adjust vapor flow resistance across the first path, or

Using control valve 70 to adjust vapor flow resistance across the second path, or

Using both valves 70 and 80 combined, depending on design criteria of F 3 and D 5.

Unlike prior art attempts, these two loops provide very wide operating ranges. The maximum available pressure drop range is being supplied by the corresponding liquid heads across the entire zones of F 3 and S 5 for valves 80 and 70 respectively as shown in FIG. 7. As manual valve 80 starts to impose an added restriction across the vapor communication line between zone B 1 and zone S 5, liquid head in line 35 communicating between zone S 5 and zone B 1 will rise to reflect the pressure difference. Therefore, the control range is almost the full height of the elevation differences. To put the pressure drop available for control into perspective, a minimum of 10 psi can be easily made available for a typical column. For those who are familiar in the art of designing thermosiphon reboilers for fractionation columns, the reasoning and design criteria should now be very clear. The same reasoning applies towards the hydraulic control and balance between zone F 3 and zone D 7 with one added variation. The liquid flow 32 from zone D 7 has to be divided between 34 and 33 going to zone F 3 and zone S 5 respectively. The following description of the liquid loops will make clear the above statement also.

FIG. 9 shows the details of the column internals around the zone D 7 liquid outlet flow 32. Liquid flow control from zone D 7 to zone F 3 as shown in FIG. 7 is effected by control valve 90. The control valve 90 is preferably located towards the lower end of the liquid leg as shown to prevent flashing on the downstream side of the control valve 90. That location also ensures that the leg is flooded at all times to give reliable liquid flow control. From the detail drawing, it is shown that the liquid 32 has to first satisfy the flow requirement 34 from flow control valve 90 and any surplus 33 will be cascaded to the next level towards zone S 3. This internal weir structure 95 eliminates the use of an additional level control loop. Liquid seal loops 99 are recommended at all liquid re-entry points to the column.

At this point, those who are familiar in the art of distillation and control should feel comfortable that the problem of flow control based on column hydraulics has been positively identified, analyzed and resolved. Furthermore, other arrangements of the above operating zones will be apparent to persons skilled in the art. Methods such as with the aid of pumps or fluid density modifying means would allow same or different elevations of the various zones, without departure from the spirit and scope of this invention. The next challenge is to take further advantage of concentration differences that would enable a even more efficient separation process.

The PETLYUK system requires that the two points of entry to and from the two columns be at the same elevation in order to avoid hydraulic imbalance. However, it may be advantageous, processwise, to return the vapor at a lower position and the liquid at a higher location due to the quality of the returning streams. PETLYUK system does not provide that flexibility unless pumps are introduced. Even so, vapor flow control would still be a very challenging task.

This invention, in contrast, provides unrestricted choice of re-entry locations, in terms of elevation, both for liquid streams entering the stripping zone as well as vapor streams entering the rectifying zone. The hydraulic limitation in the past has now been eliminated. Therefore, a more efficient separation system than previously thought possible as benchmarked by the PETLYUK system is now available. Proper process simulation can pin point the optimum vapor/liquid re-entry locations. By applying this concept to a divided wall column, the following improvements can also be realized.

Divided wall column as proposed by Wright and Giroux lack the flexibility in design to take advantage of the concentration difference. FIG. 10, within the spirit of this invention, shows the column internals that could overcome that limitation. Vapor from either side of the partition is allowed to bypass internally or externally to a higher location so that a suitable mixing location, which offers better thermodynamic efficiency, can be used. Similarly, liquid from either side of the partition can be allowed to bypass internally or externally to a lower location in the column. The vapor and liquid bypassing arrangement can be applied to any mass transfer media. External liquid bypass can be combined with arrangements shown in FIG. 9 on both sides of the partition to further increase operational flexibility by providing an on/off by-passing option.

One other built in flexibility needs to be mentioned as well. Unlike the divided wall column where the corresponding stages are essentially fixed, this invention imposes no such restriction. As much as the process designer wishes to optimize the relative separation capabilities between the prefractionation and the main column, this invention will not be hindering his or her effort. Dissimilar number of stages in the prefractionation zone and main fractionation zone offers great advantage in flexibility. A much wider separation scenarios can be covered without changing the hydraulic balance and control loop tuning set up by simply providing feed and side stream draw switching capability. That way, FIG. 7 can be switched over to FIG. 8 operation with a couple of valve swings. This invention is nothing other than truly remarkable.

Additional Ramifications

The concept of a HBFTC system as described can be extended to retrofitting existing units. Both the yield and the purity specification of a side draw stream can be enhanced by installing a partition across the middle part of an existing column. Suitable vapor and liquid internal and/or external can be provided to capture the otherwise lost thermodynamic efficiency due to mixing effect. On the other hand, a total conversion to a HBFTC system as described in this invention could also be a viable alternative, depending on economics. New columns can also be added at grade level depending on the circumstances.

This invention shows a efficient way of isolating a product cut. Each operating zone can then become a physical zone by itself, containing high product concentration. This provision opens yet another ideal avenue for reactive distillation, naturally. During the front-end design stage of any grassroots plant or debottlenecking projects, HBFTC systems can now be an important option to consider. Options that could make a sizable impact on the feasibility of the project is made available by this invention.

Conclusion, Ramifications, and Scope of Invention

Thus, the reader will see that this invention is truly one practical solution of transforming the well-known fully thermally coupled systems to a hydraulically balanced state; only an academic dream in the past. In essence, the present invention provides a practical and thermodynamically powerful alternative in the field of separation processes. While the above description contain many specificities, these should not be construed as limitations on the scope of the invention, but rather as exemplification on one preferred embodiment thereof. Many other variations are possible. Examples can be found in reactive distillation, coal tar distillation, biotechnology, cryogenic separations, pharmaceutical manufacturing processes and food and beverage applications and the list goes on.

What is claimed are the invention is:

1. A system comprising of:

An apparatus further comprising of:

1. at least one reboiler, at least one condenser, means for mass transfer in between said reboiler and said condenser,
2. means for communicating and means for rationing internal vapor traffic between desirous zones within said apparatus,
3. means for communicating and means for rationing internal liquid traffic between desirous zones within the apparatus,
4. means for placing at least one vapor stream at a suitable location within the apparatus to minimize mixing inefficiencies,
5. means for placing at least one liquid stream at a suitable location within the apparatus to minimize mixing inefficiencies,

means for maintaining hydraulic balance at changing operating conditions and control of the apparatus thereof,

to separate at least one feed stream containing at least two components, into at least one overhead distillate stream, at least one side draw stream and at least one bottom stream; each such said product stream contains different averaged volatility.

2. The apparatus according to claim 1, wherein said means for mass transfer is a trayed distillation column comprising of four discrete operating zones in ascending elevation, namely:

- A stripping zone, zone B, where a bottoms product is withdrawn,
- A prefractionation zone, zone F, where a feed stream is introduced,
- A main fractionation zone, zone S, where a side stream product is withdrawn,
- A rectifying zone, zone D, where a distillate product stream is withdrawn,

With means for communicating and means for rationing internal vapor traffic from said zone B through said zone F to said zone D, and between the zone B through the zone S to the zone D; placing the vapor streams at a suitable location within the apparatus to minimize mixing inefficiencies,

With means for communicating and means for rationing internal liquid traffic between the zone D to the zone S to the zone B, and between the zone D to the zone F to the zone B, placing the liquid streams at a suitable location within the apparatus to minimize mixing inefficiencies,

With means for maintaining hydraulic balance at changing operating conditions and control of the apparatus thereof.

3. The apparatus according to claim 2, wherein the means for communicating and means for rationing internal vapor traffic between the various zones is described as follows:

The stripping zone, zone B,

The zone B is communicated without restriction from the top of the zone B with the bottom of the zone F, one other vapor communication route enables the zone B to communicate, at the top of the zone B, with the zone S, at the bottom of zone B, through a secondary adjustable restriction means,

The prefractionation zone, zone F,

The zone F, from the top of zone F, is communicated with the zone D at a suitable location in the zone D, through a primary adjustable restriction means in between,

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The main fractionation zone, zone S,

The top of zone S is communicated without restriction with the zone D at a suitable location.

4. The apparatus according to claim 2, wherein the means for communicating internal liquid traffic between the various zones is described as follows:

The rectifying zone, zone D,

The zone D is communicated from the bottom of the zone D, without restriction, with the top of the zone S. One other liquid communication route communicates the zone D from the bottom of the zone D with the zone F, at the top of the zone F, with an adjustable restriction means to effect means of liquid flow rationing control,

The main fractionation zone, zone S,

Liquid from the zone F, at the bottom of the zone F, is communicated without restriction with the zone B at a suitable location,

The prefractionation zone, zone F,

The zone F is communicated from the bottom of the zone F, without restriction, with the zone B at a suitable location,

All liquid flow entrances described above are equipped with a liquid seal.

5. The apparatus according to claim 3, wherein said primary adjustable restriction means is an automatic flow control valve.

6. The apparatus according to claim 3, wherein said secondary adjustable restriction means is a manual butterfly valve.

7. The apparatus according to claim 4, wherein said adjustable restriction means is an automatic flow control valve.

8. The apparatus according to claim 4, wherein said means for liquid flow rationing control is comprised of 1) withdrawing one portion of a liquid stream from a column's internal liquid traffic preferably at a Downcomer location to satisfy flow requirement of said portion of said liquid stream, and 2), overflowing the liquid stream remaining across an internal weir to satisfy said rationing control.

9. A divided wall column, comprising of an internal longitudinal partition resulting in creating a prefractionation zone and a main fractionation zone, wherein an internal liquid flow, selected from one of the following groups consisting of

a liquid stream exiting from said prefractionation zone and

a liquid stream exiting from said main fractionation zone;

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is provided with means for bypassing at least one tray below said partition.

10. The apparatus according to claim 9, wherein said means for bypassing at least one tray below the partition is provided by a Downcomer extending through at least one tray below the partition.

11. The apparatus according to claim 9, wherein said means for bypassing at least one tray below the partition is provided by totally drawing off liquid from a tray at the partition and redirecting said liquid to return to the column at least one tray below the partition.

12. A divided wall column, comprising of an internal longitudinal partition resulting in creating a prefractionation zone and a main fractionation zone, wherein an internal vapor flow, selected from one of the following groups consisting of,

a vapor stream exiting from said prefractionation zone and

a vapor stream exiting from said main fractionation zone; is provided with means for bypassing at least one tray above said partition.

13. The apparatus according to claim 12, wherein said means for bypassing at least one tray above the partition is provided by a chimney tray extending through at least one tray above the partition.

14. The apparatus according to claim 12, wherein said means for bypassing at least one tray above the partition is provided by totally withdrawing said vapor from a tray at the partition and redirecting the vapor to return to the column at least one tray above the partition.

15. The apparatus according to claim 1, wherein said reboiler and said condenser are powered by a heat pump.

16. The apparatus according to claim 2, wherein at least one of the said zones B, F, D and S functions as a reactive distillation zone.

17. The apparatus according to claim 16, wherein at least one reactant feed stream is fed to said reactive distillation zone.

18. The apparatus according to claim 16, wherein at least one product feed stream is withdrawn from said reactive distillation zone.

19. The apparatus according to claim 2, wherein said means of mass transfer comprised of a combination of tray and packed bed.

20. The apparatus according to claim 19, wherein said means of mass transfer contains catalysts.

* * * * *

Multiple Steady-State Solutions for Interlinked Separation Systems

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Multiple steady-state solutions for three different types of interlinked separation systems have been discovered by using a computer simulation program that applies a differential arc-length homotopy continuation technique for solving the large sets of rigorous nonlinear modeling equations. The multiple solutions were found from multiple starting points. A degrees-of-freedom analysis and a parallel mathematical development based on the approximate group-method equations provided a basis to confirm the number of steady-state solutions and to permit prediction of the number of multiple steady-state solutions for other kinds of interlinked separation systems.

Introduction

Multiple steady-state solutions are known to occur in chemical reaction systems, fluid-flow problems, elasticity theory, and biological models, as mentioned by Jepson and Spence (1985). However, until very recently, multiple solutions had not been observed in separation systems. Usually, separation systems have been assumed to have a unique steady-state solution when the degrees of freedom of the system are satisfied. Wayburn and Seader (1984) reported what is believed to be the first instance of multiple steady-state solutions for an interlinked separation system. They studied a Petlyuk system, shown in Figure 1a, wherein a ternary mixture of benzene, toluene, and *o*-xylene at its bubble point was to be separated into three products of specified purities, for a specified reflux ratio and a specific bottoms total flow rate. Using a robust differential arc-length homotopy continuation method for rigorously solving the large set of nonlinear equations, they discovered two different sets of internal flow distributions that satisfied the desired specifications. Their surprising observation induced a more detailed exploration of the Petlyuk system in order to discover any other solutions that might exist. In addition, it was desirable to seek multiple solutions for other popular interlinked separation systems like those shown in Figure 1b,c for a fractionator with a side-cut reboiled stripper and a fractionator with a side-cut refluxed rectifier, respectively. It was also desired to determine the causes that motivated the occurrence of multiple solutions in those systems in order to predict their possible incidence for other separation-system configurations.

All the computer runs for this study were made using the COFRAC program written for a mainframe computer by Wayburn (1983) and adapted for use on a minicomputer by Chavez (1985). The mixture studied (benzene, toluene, and *o*-xylene) was nearly ideal. Accordingly, *K* values were obtained from Raoult's law by using the Antoine equation for vapor pressure. Enthalpies were calculated by using a five-term polynomial for C_p of the vapor and the Clausius-Clapeyron equation for the heat of vaporization, which was needed to obtain liquid enthalpies.

To solve the large set of defining nonlinear equations, $F(x) = 0$, for the system, COFRAC solves a corresponding homotopy equation

$$H(x,t) = tF(x) + (1-t)[F(x) - F(x^0)] = 0 \quad (1) \\ t \in [0,1], \quad x \in R^n$$

by starting from an initial point $(x,t) = (x^0,0) \in R^{n+1}$, differentiating eq 1 with respect to the arc length of the path connecting $F(x) = F(x^0)$ to $F(x) = 0$, and solving the resulting initial-value problem in ordinary differential equations. The Leray-Schauder theorem guarantees the existence of the path, making the differential arc-length homotopy continuation method robust from any initial starting point.

Problem Definition

The three cases studied here each utilized the following single-feed specifications: 200 kg-mol/h of benzene, 400 kg-mol/h of toluene, 400 kg-mol/h of *o*-xylene, 383.4 K (bubble point temperature), and 101.3 kPa.

The following general assumptions applied to each of the three cases:

1. The reflux divider and all stages, except condensers and reboilers, are considered adiabatic.
2. Heat-transfer rates for condensers and reboilers are never specified.
3. The system operates at atmospheric pressure (101.33 kPa) with zero pressure drop throughout the system.
4. The configuration of the system, i.e., number of stages and location of feeds, side streams, and interlinks, is known.
5. The composition and condition of the feed are known as given above.
6. All product streams leave the system as saturated liquids.

Although the initial plan was to provide the same total number of theoretical stages for each of the three interlinked systems studied in order to compare the three separation schemes, the appearance of pinch zones discouraged this idea and the systems in Figure 1b,c were configured with smaller numbers of stages at the expense of higher reflux ratios. In performing the calculations for each system, we considered the combination formed by the total condenser and the reflux divider to be a stage, following the technique of Naphtali and Sandholm (1971).

The following is a discussion of each of the three interlinked systems mentioned above and referred to hereafter as cases 1, 2, and 3.

Case 1. Petlyuk System

The configuration of case 1, represented schematically in Figure 1a, corresponds exactly to that of case IV of Wayburn and Seader (1984) and was used to initiate this study. The system consists of a 20-stage prefractionator

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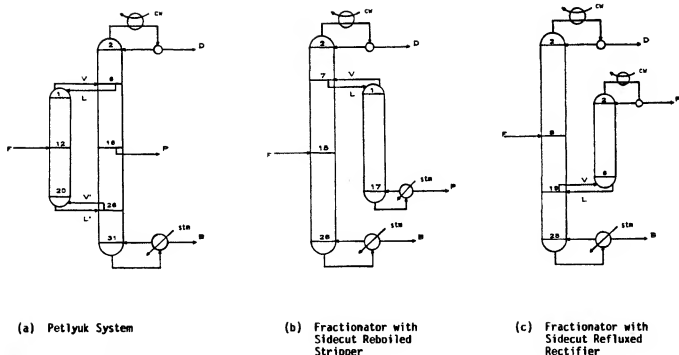


Figure 1. Interlinked separation systems.

interlinked with a 32-stage fractionator. The latter includes a total condenser and a partial reboiler. The stage locations for the feed, products, and interlinks are all included in Figure 1a.

In order to determine the number of required specifications, a degrees-of-freedom analysis was performed in the manner described by Henley and Seader (1981). Table I presents the degrees of freedom for each of the elementary units that comprise the system. When these are summed and corrected for the effect of the interconnecting streams between the units, the resulting total degrees of freedom of the system is $2(M + N) + C + 14$, where $N = 20$ is the total number of equilibrium stages in the prefractionator and M is 32, the total number of stages in the fractionator, including condenser and reboiler. Table II lists the implicit specification for the problem, based on the general assumptions stated above, and the corresponding degrees of freedom consumed. The five degrees of freedom remaining were consumed by the following additional specifications: molar purity of benzene in the distillate, 95%; molar purity of toluene in the middle product, 90%; molar purity of *o*-xylene in the bottoms, 95%; total bottoms flow rate, 380 kg-mol/h; reflux ratio, values in the range from 4.525 to 5.75. If we assume that the benzene does not appear in the bottoms and the xylene does not appear in the distillate, the purity specifications can be achieved by specifying any value of the total bottoms flow rate in the range from 377.7 to 421.04 kg-mol/h, as can be shown by a mass balance. The value of 380 kg-mol/h was chosen for compatibility with the example of Wayburn and Seader (1984). The difference in the above specifications and those of Wayburn and Seader is that the latter only studied a reflux ratio of 5.75, while a range of values is examined here.

The COFRAC program requires starting guesses only for stream total molar flow rates and stage temperatures. The remaining starting guesses are provided by COFRAC, as described by Wayburn and Seader (1984). Starting guesses for the flow rates were based on a molar flow rate of 410 kg-mol/h for the middle product; since a bottoms flow rate of 380 kg-mol/h was specified, a global mass balance results in a distillate rate of 210 kg-mol/h. Subcases were

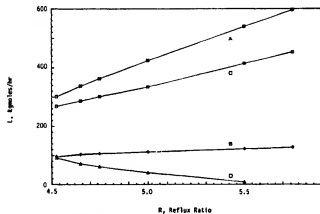


Figure 2. Case 1. Multiple solutions for liquid interlink flow rate.

run for each of six specified reflux ratios within the range cited above by using, for each reflux ratio, a range of guesses for the interlinking streams, L and V . Starting guesses for L varied from 100 to 500 kg-mol/h and for V from 100 to 1000 kg-mol/h. The remaining internal-stream flow rates were estimated under the assumption of constant molar overflow.

Stage temperatures were estimated for the fractionator by using the boiling point temperature of pure benzene for the condenser and of pure *o*-xylene for the reboiler; the remaining stage temperatures of the fractionator were then estimated by linear interpolation between the top and bottom temperatures. The temperatures of the top and bottom stages of the prefractionator were assumed to be the same as the temperatures of corresponding interlinking stages in the fractionator, and another linear interpolation was made between those two temperatures to estimate the remainder of the stages in the prefractionator.

The technique used to search for multiple solutions involved an exhaustive search from all physically possible combinations of starting guesses for the total molar flow rates of the interlinking streams, L and V , in Figure 1a. This use of multiple starting points was the technique that initially led Wayburn and Seader (1984) to discover additional solutions.

Table I. Degrees of Freedom for System of Case 1

PREFRACTIONATOR:

N_1 -stage cascade (Stages 1 to 11)	$2N_1$	+	$2C + 5$
Feed stage (stage 12)			$3C + 8$
N_2 -stage cascade (Stages 13 to 20)	$2N_2$	+	$2C + 5$
<hr/>			
SUM	$2(N_1 + N_2)$	+	$7C + 18$
Correction for 4 redundant streams		-	$4C - 8$
<hr/>			
Total	$2(N_1 + N_2)$	+	$3C + 10$
DEGREES OF FREEDOM (Prefractionator)	$2N + 3C + 8$	*	

FRACTIONATOR:

Total condenser (stage 1)			$C + 4$
Reflux divider (stage 1)			$C + 5$
M_1 -stage cascade (stages 2 to 5)	$2M_1$	+	$2C + 5$
Interlinking stage (stage 6)			$3C + 9$
M_2 -stage cascade (stages 7 to 15)	$2M_2$	+	$2C + 5$
Stage with sidestream (stage 16)			$2C + 7$
M_3 -stage cascade (stages 17 to 25)	$2M_3$	+	$2C + 5$
Interlinking stage (stage 26)			$3C + 9$
M_4 -stage cascade (stages 27 to 31)	$2M_4$	+	$2C + 5$
Partial Reboiler (stage 32)			$C + 4$
<hr/>			
SUM	$2(M_1 + M_2 + M_3 + M_4)$	+	$19C + 58$
Correction for 17 Redundant streams		-	$17C - 34$
<hr/>			
Total	$2(M_1 + M_2 + M_3 + M_4)$	+	$2C + 24$
DEGREES OF FREEDOM (Fractionator)	$2M + 2C + 14$	**	

COMPLETE SYSTEM:

Prefractionator	$2N + 3C + 8$
Fractionator	$2M + 2C + 14$
SUM	$(N+M) + 5C + 22$
Correction for 4 redundant streams	$- 4C - 8$
<hr/>	
DEGREES OF FREEDOM	$2(N+M) + C + 14^*$

* $N = N_1 + N_2 + 1$ (cascades plus the feed stage)** $M = M_1 + M_2 + M_3 + M_4 + 5$ (Cascades plus condenser, 2 interlinking stages, sidestream stage and reboiler).

Table II. Implicit Specifications for Case 1*

heat transfer to/from all stages and divider, except condenser and reboiler (1, 2)	$M + N - 1$
pressure of all stages including condenser, reboiler, and reflux divider (3)	$M + N + 1$
degrees of subcooling in total condenser (6)	1
component flow rates, temperature, and pressure of the feed (5)	$C + 2$
number of stages in each column (4)	2
feed location (4)	1
location of the interlinking stages and stage with a side stream (4)	3
sum	$2(M + N) + C + 9$

*Numbers in parentheses indicate the general assumptions that imply the specification.

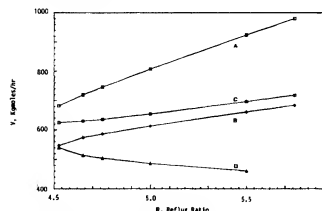


Figure 3. Case 1. Multiple solutions for vapor interlink flow rate.

Four solutions, referred to as solutions A, B, C, and D, were discovered for the Petlyuk system. Figures 2 and 3 present the converged values of the liquid and vapor interlink flow rates, L and V , for each of the four solutions over the range of reflux ratios studied. It can be observed in Figure 2 that, at a reflux ratio of 5.75, only three solutions exist because the missing solution D, incurs a negative value for L . It may also be observed that, at reflux ratios lower than about 4.525, solutions B and D converge to each other. Several runs made at a lower reflux ratio of 4.50 were unsuccessful in finding any solution, and therefore it is assumed that, at some reflux ratio between 4.50 and 4.525, solutions A and C converge to each other to form a unique solution to the system. These two points of convergence represent minimum reflux points, below which physical solutions are not possible. Solutions A and B for a reflux ratio of 5.75 were the ones reported by Wayburn and Seader (1984).

Table III includes a comparison, for a reflux ratio of 5.00, of a more extensive set of converged molar flow rates for the four different solutions. It can be observed that, although the flow rates of liquid streams, L and L_6 , and vapor streams, V and V_7 , are each different for each solution, the sums, $L + L_6$ (the total liquid flow leaving the top section of the fractionator) and $V + V_7$ (the total vapor flow rate entering the same top section), are almost identical for solutions A and C and for solutions B and D. It is important to note that the states of streams L and L_6 and of streams V and V_7 are each identical because each pair of streams originates from the same stage in the system. Therefore, in the upper section of the system, from the condenser down to the interlinking stage (stage 6), solutions A and C and solutions B and D each differ from each other only in the side-stream ratio of the interlinking stage (stage 6).

A similar situation can be observed in the lower section of the fractionator, from the partial reboiler up to the

Table III. Partial Results for Case 1 at $R = 5.00$

stream	flow rates, kg-mol/h, for solutions			
	A	B	C	D
D	208.23	208.22	208.23	208.22
L	423.66	111.61	337.54	40.68
L_6	542.53	828.17	628.70	899.39
$L + L_6$	966.19	939.78	966.24	940.07
V	808.36	613.82	654.96	486.72
V_7	366.06	534.19	519.51	661.57
$V + V_7$	1174.42	1148.01	1174.47	1148.29
P	411.76	411.76	411.76	411.77
L'	1399.68	1115.14	1319.98	1047.94
L_{25}	109.32	393.30	187.88	460.08
$L' + L_{25}$	1509.00	1508.04	1507.86	1508.02
V'	784.38	617.34	637.40	493.98
$S_{26}V'$	344.62	511.67	490.45	634.03
$V' + S_{26}V'$	1129.00	1129.01	1127.85	1128.01
B^a	380.00	380.00	380.00	380.00

*Specified.

interlinking stage (stage 26), where solutions A and B have almost identical sums, $L' + L_{25}$ and $V' + S_{26}L'$, as do solutions C and D. This characteristic of the multiple solutions suggests the existence of some interaction between the prefractionator and the middle section of the fractionator to provide an adequate input into the far upper and far lower sections of stages to the fractionator.

The use of Newton's method proved to be satisfactory from most starting points. However, Newton's method failed to converge to solution C at reflux ratios of 4.525, 4.55, and 4.65, i.e., the lower reflux ratios of the range. Accordingly, the continuation method was employed successfully in those cases. After these solutions were obtained, Newton's method was tried again with better starting guesses and it converged to all three points. Thus, the globally convergent nature of the continuation method and the locally convergent nature of Newton's method were demonstrated.

The occurrence of more than one real solution for a physical two-phase multicomponent, multistage separation system was surprising because the restrictions imposed by the specifications (e.g., positive flow rates and molar fractions) would intuitively be expected to prevent multiple solutions. In order to test the influence of the choice of specifications on the occurrence of multiple solutions, a local degrees-of-freedom analysis was made, following the philosophy of the sequential modular approach to steady-state simulation (Westerberg et al., 1979) wherein the local degrees-of-freedom analysis is made by assuming initially that properties of input streams to a particular unit of the system are known and, if the unit appears overspecified, some of the variables assumed known are set free.

Following the sequential modular approach down from the total condenser of the fractionator in Figure 1a and referring to Table I, it is observed that the total degrees of freedom for the total condenser of the fractionator is $C + 4$. By assuming that the input stream to the condenser is known, two degrees of freedom remain unused. Those are consumed by the specification of the condenser pressure and degrees of subcooling of the condensate. Therefore, the local degrees of freedom (DOF) of the condenser are satisfied.

The DOF of the reflux divider are $C + 5$, but $C + 2$ are consumed if the divider input is assumed known. The remaining degrees of freedom are consumed by the specification of the divider pressure, heat-transfer rate (zero), and reflux ratio. However, an extra specification is associated with the divider, namely, the purity of benzene in the distillate output stream, D . Thus, in order to avoid

overspecification, one variable must be set free somewhere else in the system.

The M_1 -stage equilibrium cascade of the fractionator, which contains stages 2-5, has a total DOF of $2M_1 + 2C + 5$. The specification of the heat-transfer rate and pressure of each stage consumes $2M_1$ degrees of freedom. Specification of the number of stages uses one more, leaving $2C + 4$ available, which correspond to the two streams entering the cascade. However, the one variable set free in the divider must be propagated.

The next unit of the system is the top interlinking stage (stage 6), which has $3C + 9$ degrees of freedom. Assuming that the pressure, the heat-transfer rate, and the three input streams to the stage are known, $3C + 8$ degrees of freedom are consumed, leaving only one DOF available. Normally this would be used by the side-stream ratio specification, which in this case is not specified and, therefore, becomes the variable set free by the purity specification in the divider and is propagated. In consequence, the upper section of the fractionator, including stage 6, satisfies its degrees of freedom, provided that the two vapor streams entering the top interlinking stage are completely known and the side-stream ratio is a computed variable.

The upper section of the prefractionator (stages 1-11) has a total of $2N_1 + 2C + 5$ degrees of freedom. As before, $2N_1 + 1$ degrees are consumed by the pressure and heat-transfer rate specifications for each stage and by the number of stages, leaving a total of $2C + 4$ degrees of freedom to be used. If, consistent with the sequential modular approach, the two input streams to the section are assumed known, the local degrees of freedom are satisfied and the unknowns associated with the two streams leaving the cascade can be calculated. However, since the side-stream ratio of the interlinking stage is not known, only the composition, pressure, and temperature of the liquid stream, L , can be assumed known and not the total flow rate L . Therefore, this cascade is undetermined by one degree of freedom.

It is obvious that the section of the fractionator between, but excluding, the interlinking stage and the middle product stage presents an entirely similar situation. Since the total flow rate of the liquid stream, L , cannot be assumed known, this cascade is undetermined by one degree of freedom.

Since these latter two cascades must somehow satisfy the degrees-of-freedom analysis, some other implicit specifications must exist. Such specifications are as follows: (1) the composition of the two liquid streams entering each of the cascades is the same (since they proceed from the same original stream), and (2) the sum of the flow rates of these two liquid streams must equal the flow rate of the total liquid leaving the interlinking stage. These specifications involve both cascades in an interactive manner, which reinforces the hypothesis that multiple solutions originate by the interaction of parallel cascades.

If the system is examined up from the partial reboiler of the fractionator, a situation entirely similar to that of the upper sections occurs. The reboiler has $C + 4$ degrees of freedom, with three consumed by the pressure, purity of xylene, and total bottoms flow rate. Therefore, if the input stream to the reboiler is assumed known, consuming $C + 2$ more degrees of freedom, then the reboiler would be overspecified. This is equivalent to the overspecification of the reflux divider, and the structure of the system below the feed and middle product stages is exactly equivalent to the upper sections already examined. In consequence, interaction of parallel equilibrium cascades under the

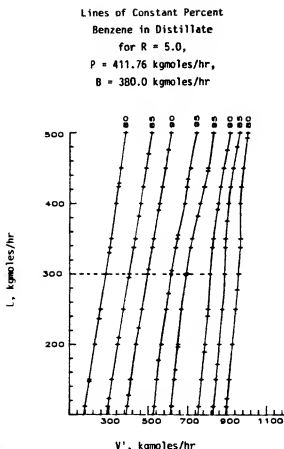


Figure 4. Case 1. Lines of constant benzene purity.

middle product of the fractionator and under the feed stage of the prefractionator occurs.

A second set of specifications was constructed, seeking to satisfy the local degrees of freedom of every single section of the system, in order to determine the effect of sharing specifications on the appearance of multiple solutions. The values of the specifications were the following: (1) reflux ratio, $R = 5.00$; (2) bottoms flow rate, $B = 380.0$ kg-mol/h; (3) middle product flow rate, $P = 411.76$ kg-mol/h; (4) liquid interlink flow rate, L , equal to a set of values; (5) vapor interlink flow rate, V' , equal to a set of values.

The middle product flow rate was set to 411.76 kg-mol/h because, as observed by Chavez (1985), this value is always the same for the purity specifications given in the first set of specifications. The interlink flow rates, L and V' , were given values that spanned the range from 100 to 500 kg-mol/h for L and from 100 to 1200 kg-mol/h for V' . In this case only one reflux ratio was studied, since the results are, in all probability, applicable to the other reflux ratios as well.

In order to increase the chances of Newton's method to converge, the computer runs were made sequentially for the sets of L and V' values, using the results of one run to provide the starting guesses for the next run. Except for a few points that involved low internal traffic, i.e., column nearly dry, Newton's method performed satisfactorily. In the few cases where Newton's method failed, the continuation method was successfully applied.

Figures 4, 5, and 6 represent curves of constant purity of benzene in the distillate, toluene in the middle product, and *o*-xylene in the bottoms, respectively. These graphs were obtained by linear interpolation of the numerical results given in detail by Chavez (1985). Figure 7 contains the constant-purity lines corresponding to the purity specifications of the first set of specifications. The four

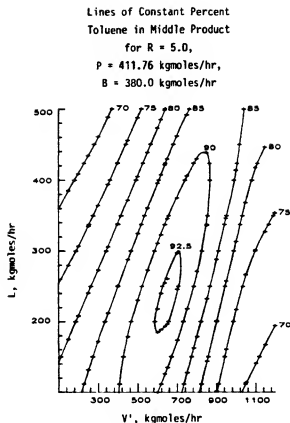


Figure 5. Case 1. Lines of constant toluene purity.

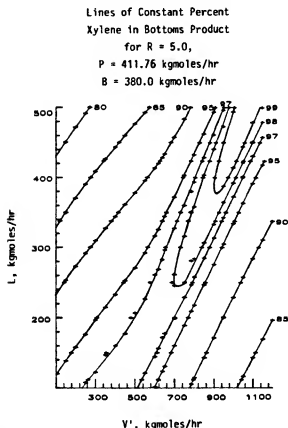


Figure 6. Case 1. Lines of constant xylene purity.

solutions are clearly observed in the intersections of the three curves. Solution D did not fall in the range tested, but its position could be inferred from the trends of the curves of Figure 7 and from the results shown in Figures 2 and 3.

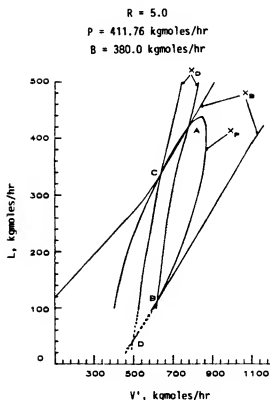


Figure 7. Case 1. Multiple solutions by intersections.

Table IV. Implicit Specifications for Case 2^a

heat transfer to/from all stages	$M + N - 2$
including reflux divider, but excluding condenser and reboilers (1, 2)	
pressure of all stages including condenser, reboilers, and reflux divider (3)	$M + N + 1$
degrees of subcooling in total condenser (5)	1
component flow rates, temperature, and pressure of the feed (5)	$C + 2$
number of stages in each column (4)	2
feed stage location (4)	1
interlinking stage location (4)	1
sum	$2(M + N) + C + 6$

^a Numbers in parentheses indicate the assumptions that imply the specifications.

An important use that can be made of Figures 4-6 is to predict what would happen if only one of the interlinks was specified and the other was not. If, for example, the specifications were $L = 300$ kg-mol/h, $P = 411.76$ kg-mol/h, $B = 380$ kg-mol/h, $x_D = 0.95$, and $R = 5$, then the solution for the vapor interlink flow rate, V' , can be obtained from Figure 4, by finding the intersection of the 95% curves with a line drawn horizontally from $L = 300$. It is clear that only two different solutions can satisfy the given specifications. If other similar specifications are used, specifying either L or V' , it can be observed that two solutions, at most, can be obtained for any given set of specifications. This observation is very important and confirms the theory presented in the next section.

Case 2. Fractionator with Side-Cut Reboiled Stripper

The system used for case 2 is shown schematically in Figure 1b. It contains a 27-stage fractionator, including a total condenser and a partial reboiler, interlinked with an 18-stage reboiled stripper, where the partial reboiler of the stripper counts as a stage. As shown by Chavez (1985), the total degrees of freedom of the system equals $2(N +$

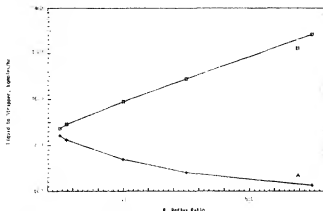


Figure 8. Case 2. Multiple solutions for liquid interlink flow rate.

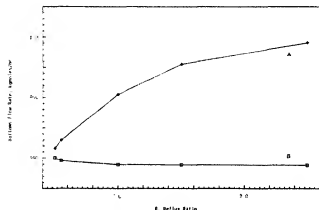


Figure 9. Case 2. Multiple solutions for bottoms flow rate.

$M) + C + 10$. Table IV shows the specifications implied by the general assumptions and the number of degrees of freedom that they consume. The values of the four remaining specifications were as follows: (1) purity of benzene in the distillate, 95%; (2) purity of toluene in the middle product; 90%; (3) purity of xylene in the bottoms, 95%; (4) reflux ratio, five values in the range from 6.5 to 8.5. Since the number of degrees of freedom for this case is one less than for case 1, the specification of the total bottoms flow rate was omitted.

The maximum value of the reflux ratio was fixed at 8.5 because at higher reflux ratios pinch zones started to appear. At reflux ratios lower than approximately 6.5 no solutions could be found. The starting guesses, which were generated in a manner similar to those for case 1, were based on the same value of 410 kg-mol/h for the middle product flow rate and assumed values for the liquid interlink flow rate, L , and the bottoms flow rate, B . The values used for L were from 800 to 1200 kg-mol/h and for B from 370 to 420 kg-mol/h. The estimate for the distillate flow rate was obtained from a global mass balance, and the remainder of the internal streams were estimated under the assumption of constant molar overflow. The temperatures were estimated in the manner described above for case 1.

Two different solutions, referred to as solutions A and B, were found for this set of specifications. Graphical representation of the values of L and B for the reflux ratios tested is presented in Figures 8 and 9.

Solution B could not be found with Newton's method for the given specifications, even when very good starting guesses for the flow rates of the interlink and bottom streams were provided. All computer runs that used Newton's method either converged to solution A or failed to converge. The continuation method converged to so-

Table V. Partial Results for Case Study 2 at $R = 7.00$

variable	solution	
	A	B
D , kg-mol/h	187.16	210.32
% benzene in V_7	37.2	37.1
L , kg-mol/h	459.73	349.20
L_7 , kg-mol/h	739.21	990.00
$L + L_7$, kg-mol/h	1198.94	1339.20
V , kg-mol/h	327.45	578.24
V_{26} , kg-mol/h	1058.66	971.29
$V + V_{26}$, kg-mol/h	1386.11	1549.53
% toluene in L	77.6	75.81
P , kg-mol/h	411.76	411.76
Q_{25} , kW	1451.56	2575.96
% xylene in L_7	2.94	5.04
B , kg-mol/h	401.08	377.91
Q_{45} , kW	4900.03	4534.80

lution B when a nearly dry condition (low liquid traffic) was assumed for the fractionator. Since not all possible starting guesses were used in this part of the study, it cannot be guaranteed that Newton's method will fail to find solution B for all starting guesses. It must be clear also that starting guesses were provided only for selected stages and only for total flow rates. The possibilities of convergence might be increased if starting guesses were given for component molar flows for every stage.

Table V presents a comparison of some of the most important variables for each of the two solutions at $R = 7.0$. It is observed that, although the total flow rates of the streams of the upper section of the system are not equal, the mole fractions are stagewise correspondent between the two solutions. This fact indicates the possible interaction of the two parallel sections of the system, located below the interlinking stage, to provide an adequate input to the upper section in a manner similar to that of case 1.

A local degrees-of-freedom analysis was necessary to determine whether the same conditions found in case 1 were also present in case 2. By inspection, it is obvious that the upper section of the system of Figure 1b has the same configuration as the upper section of the system of case 1, shown in Figure 1a. As before the apparent overspecification of the reflux divider, caused by the specification of the reflux ratio and the purity of benzene in the distillate, is propagated to the interlinking stage, which becomes completely determined, assuming that the vapor streams entering the interlinking stages are known.

The lower sections of the system resemble the intermediate sections of the system of Figure 1a, and therefore, to satisfy their local degrees of freedom, they must share the implicit specifications that (1) the sum of the flow rate of the liquid streams entering stage 8 of the fractionator and stage 1 of the stripper is equal to the total flow rate of liquid leaving the interlinking stage and (2) the compositions of those three liquid streams are identical.

Following the same method used in case 1, the following second set of specifications was devised to satisfy the local degrees of freedom of every single unit of the system: (1) reflux ratio, $R = 7.0$; (2) middle product flow rate, $P = 411.76$ kg-mol/h; (3) interlink stream flow rate L over a range of values; (4) bottoms flow rate B over a range of values.

Several runs were made using values of B from 370 to 420 kg-mol/h and for L from 500 to 1200 kg-mol/h. Plots of B vs. L for lines of constant product purity, similar to Figures 4-6 for case 1, were prepared and are given by Chavez (1985). Figure 10 contains the curves that correspond to the purity specifications of the first set of specifications, i.e., 95% benzene in the distillate, 90% toluene

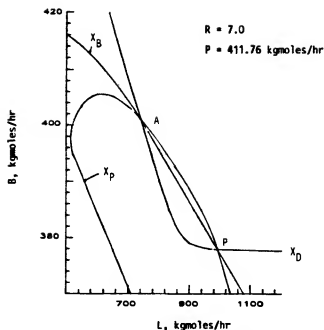


Figure 10. Case 2. Multiple solutions by intersections.

in the middle product, and 95% xylene in the bottoms. Solutions A and B are shown in Figure 10 at the point where the three curves intersect each other. It can be observed that solution B is located near the knee of the benzene curve, and that may have been the reason why Newton's method converged to solution A, even when very good starting guesses to solution B were provided.

Case 3. Fractionator with Side-Cut Refluxed Rectifier

The system corresponding to this case is shown schematically in Figure 1c. The total degrees of freedom is given by Chavez (1985) as $2(N + M) + C + 13$. The number of specifications implied by the general assumptions is given by Chavez (1985) as $2(M + N) + C + 9$. As in the two previous cases, two different sets of specifications were used to consume the remaining four degrees of freedom. The following values applied to the first set of specifications: (1) purity of benzene in the distillate, 95%; (2) purity of toluene in the middle product, 90%; (3) purity of xylene in the bottoms, 95%; (4) reflux ratio of the fractionator, a range of values from 2.85 to 5. The total number of stages for this case was only 35 in order to avoid pinch zones. The procedure to estimate the starting guesses was similar to that used for case 2.

Only one solution was found for this case. Since the system of this case bears characteristics entirely similar to those of case 2, the appearance of a second solution was expected. To ensure that all possible solutions were found is combinatorially impossible because, as indicated by the behavior of solution B in case 2, there may be solutions for which convergence is very difficult. Therefore, a second set of specifications was employed either to confirm that no other solutions existed or to estimate the location of a second solution. The values used were as follows: (1) reflux ratio, $R = 5$; (2) middle product flow rate, $P = 411.76$ kg-mol/h; (3) interlink stream flow rate V over a range of values; (4) bottoms flow rate B over a range of values. Values of the vapor interlink flow rate were in the range from 450 to 1200 kg-mol/h and from 370 to 420 kg-mol/h for the bottoms flow rate.

As for cases 1 and 2, plots of V vs. B were prepared with constant-purity lines corresponding to benzene in the distillate, toluene in the middle product, and xylene in the

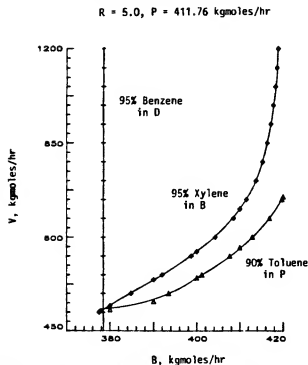


Figure 11. Case 3. Multiple solutions by intersections.

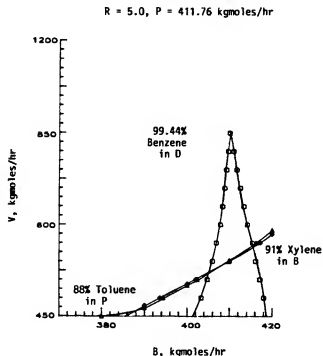


Figure 12. Case 3. A set of purity specifications that may involve multiple solutions.

bottoms, as given by Chavez (1985). The contour lines corresponding to the purity specifications of the first set are presented together in Figure 11. It is clear that the lines intersect each other only at one point, indicating a unique solution to the system for that set of specifications.

The shape of the contour line for 99.44% of benzene in the distillate and the fact that some of the contour lines for toluene and xylene follow similar trends suggest that two different solutions may exist for a set of specifications similar to the first set above, but with alternative values for the purity specifications. Figure 12 represents a set of purity specifications for which the appearance of two solutions seems feasible. The third set of specifications was the following: (1) purity of benzene in the distillate,

Table VI. Partial Results for Case 3 at $R = 5.00$

variable	solution	
	B	C
D , kg-mol/h	186.37	171.67
% benzene in D	99.44	99.44
V , kg-mol/h	547.01	651.30
V_{25} , kg-mol/h	1018.70	936.12
$V + V_{25}$, kg-mol/h	1565.71	1587.42
L , kg-mol/h	134.69	240.56
L_{10} , kg-mol/h	1832.32	1764.44
$L + L_{10}$, kg-mol/h	1967.01	2005.00
% benzene in V_{25}	2.94	5.21
% toluene in V_{25}	69.26	67.93
P , kg-mol/h	412.31	410.74
% toluene in P	88.00	88.00
R_{19}	0.34	0.61
L_{25}	1968.55	2007.82
% xylene in L_{25}	29.68	30.17
B , kg-mol/h	401.31	417.58
% xylene in B	91.00	91.00

99.44%; (2) purity of toluene in the middle product, 88%; (3) purity of xylene in the bottoms, 91%; (4) reflux ratio of the fractionator, 5.

Only one reflux ratio was studied in this case. The starting guesses for B and V were chosen near the suspected locations of the two solutions.

As expected, two different solutions were found, and a summary of results for some of the more important variables is presented in Table VI. The characteristics of the two solutions are entirely similar to those of the solutions of case 2; namely, the compositions of the internal streams in the lower section of the fractionator, from the interlinking stage to the reboiler, are identical for corresponding stages in the two solutions.

From the above three case studies, it is possible to conclude, in a preliminary manner, that appearance of multiple solutions may occur in interlinked separations systems whenever two or more sections of the system have to share specifications in order to satisfy local degrees of freedom. However, depending on the actual values of the specifications, some of those systems may have only one physically meaningful solution or none at all. The maximum number of solutions for a given interlinked configuration may depend on the number of shared specifications.

Approximate Mathematical Analysis of the Existence of Multiple Solutions

It has been shown above, by computer case studies with a rigorous mathematical model, that multiple solutions were found when local degrees of freedom for some sections of the system were not satisfied. In this section, an approximate mathematical analysis is developed to predict the existence of multiple solutions. This is accomplished by developing an approximate model that leads to a polynomial equation, the nature of whose roots can be determined by Descartes rule of signs.

The approximate analysis method selected was the Kremser (1930) group method, as applied to complex systems by Edmister (1957) and described by Henley and Seader (1981). This method seemed suitable for deriving equations that could be readily manipulated so as to show the possibility of more than one solution.

The first attempt was to derive the group-method equations for an entire interlinked system such as the Petlyuk towers. However, the resulting equations were unwieldy and very difficult to manipulate. Therefore, a reduced approach was developed wherein group-method equations were formulated for just that portion of the

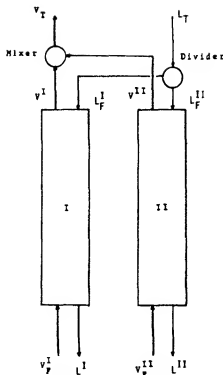


Figure 13. Parallel equilibrium cascades for approximate mathematical analysis.

system where local degrees of freedom are not satisfied individually.

The system of Figure 13 is an arrangement of two interlinked columns, which may represent any of the interlinked sections of the three case studies presented above. The stream symbols in Figure 13 represent total molar flow rates; corresponding lower case letters will represent component molar flow rates. Columns I and II each contain a single cascade with arbitrary numbers of equilibrium stages, N and M , respectively. Separate vapor feeds, V_F^I and V_F^{II} , are introduced to the bottom of each column. The total liquid feed, L_T , at the top of the system is divided between the two columns to provide the local liquid feeds, L_F^I and L_F^{II} . The quantitative distribution of these two liquid streams is given by the divider split ratio, $s = L_F^I/L_T$. Two liquid products, L^I and L^{II} , are obtained from the bottom, and two vapor products, V^I and V^{II} , are obtained from the top of each column. Streams V^I and V^{II} are combined to obtain a single vapor product, V_T , for the entire system. It is assumed, as in the three cases above, that the pressure and heat-transfer rates are given and that the number of stages of each column is also known. It is also possible to assume without loss of generality that all the streams entering the system, i.e., V_F^I , V_F^{II} , and L_T , are completely specified.

The local degrees of freedom for each of the columns and for the mixer and divider are obtained, as before, by using the method explained by Henley and Seader (1981). The degrees of freedom of column I equal $2N + 2C + 5$. If the pressure and heat-transfer rate for each stage and the number of stages N are specified, $2N + 1$ degrees of freedom are used. The complete specification of the vapor feed, V_F^I , uses $C + 2$ degrees more, and the remaining $C + 2$ degrees of freedom will be consumed if the liquid feed, L_F^I , is also completely specified. Column II presents entirely similar circumstances, and therefore, its local degrees of freedom will be satisfied if the liquid stream, L_F^{II} , is also completely specified.

The degrees-of-freedom analysis for the entire system is as follows:

column I	$2N + 2C + 5$
column II	$2M + 2C + 5$
mixer	$2C + 5$
divider	$C + 4$
total	$\frac{2(M+N) + 7C + 19}{-4(C+2)}$
correction for 4 redundant streams	
degrees of freedom	$2(M+N) + 3C + 11$

A total of $2(M+N) + 2$ degrees of freedom is used by specifying the pressure and heat-transfer rates for all stages and for the mixer and divider, and two more by specifying the number of stages M and N . The two vapor feeds, V_F^I and V_F^{II} , and the liquid feed, L_T , are assumed completely specified; therefore, $3C + 6$ more degrees are used, for a total of $2(M+N) + 3C + 10$.

The remaining specification will determine whether or not the local degrees of freedom are satisfied by every section of the system. If the divider split ratio is specified, both L_F^I and L_F^{II} streams become completely specified and the local degrees of freedom of both columns are satisfied and a unique solution could be expected. However, if the total vapor flow rate, V_T , or a component flow rate, v_T , is specified instead, the degrees of freedom are satisfied only when columns I and II are considered together, because, as explained above, the remaining degrees of freedom are satisfied by the restriction imposed by the component material balances around the divider and the mixer, i.e.

$$L_T = L_F^I + L_F^{II} \quad (2)$$

$$V_T = V^I + V^{II} \quad (3)$$

Similar equations apply for each component. The case in which the split ratio is not specified is equivalent, in terms of degrees of freedom, to the cases where multiple solutions appeared.

The Kremser method utilizes the definition of the component absorption and stripping factors for a single equilibrium stage as

$$A_i = L/K_i V \quad (4)$$

and

$$S_i = K_i V/L \quad (5)$$

where L and V are the total molar flow rates leaving the stage and K_i is the phase-equilibrium coefficient for component i . The recovery functions for a given component in a single column are defined as follows

$$\phi_A = v_{\text{out}}/v_{\text{in}} \quad (6)$$

$$\phi_S = l_{\text{out}}/l_{\text{in}} \quad (7)$$

where ϕ_A represents the fraction of the component flow rate in the entering vapor that is not absorbed. Likewise, ϕ_S is the fraction of the component flow rate in the entering liquid that is not stripped.

Applying eq 6 and 7 to the entire system shown in Figure 13, for any component, yields

$$(v_T)_{\text{abs}} = v_F^I \phi_A^I + v_F^{II} \phi_A^{II} \quad (8)$$

and

$$l^I = l_F^I \phi_S^I \quad (9)$$

$$l^{II} = l_F^{II} \phi_S^{II} \quad (10)$$

where it is important to note that eq 8 assumes that a component being absorbed from V_F is not present in the entering liquid. Correspondingly, eq 9 and 10 assume that a component being stripped from l_F is not present in the entering vapor. For components which appear in both the

entering vapor and entering liquid, the overall contributions to v_T can be obtained by adding eq 8 to the following equivalent of eq 9 and 10

$$(v_T)_{\text{str}} = l_F^I(1 - \phi_S^I) + l_F^{II}(1 - \phi_S^{II}) \quad (11)$$

to give

$$v_T = (v_T)_{\text{abs}} + (v_T)_{\text{str}} \\ = v_F^I \phi_A^I + v_F^{II} \phi_A^{II} + l_F^I(1 - \phi_S^I) + l_F^{II}(1 - \phi_S^{II}) \quad (12)$$

The recovery functions, ϕ_A and ϕ_S , for a given component are given by Kremser in terms of effective average absorption and stripping factors as

$$\phi_A = \frac{A_e - 1}{A_e^{N+1} - 1} \quad (13)$$

$$\phi_S = \frac{S_e - 1}{S_e^{N+1} - 1} \quad (14)$$

Assume that A_e and S_e for stage sections I and II are given by eq 4 and 5 with L and V set equal to the flow rates entering the sections and K set equal to some average value. In addition, extend the definition of the split fraction to give

$$s = l_F^I/l_T = L_F^I/L_T \quad (15)$$

and

$$1 - s = l_F^{II}/l_T = L_F^{II}/L_T \quad (16)$$

If eq 12-16 are combined, the following expression for v_T is obtained:

$$v_T = v_F^I \frac{\left(\frac{sL_T}{K^I V_F^I}\right)^{N+1} - 1}{\left(\frac{sL_T}{K^I V_F^I}\right)^{N+1} - 1} + v_F^{II} \frac{\left(\frac{(1-s)L_T}{K^{II} V_F^{II}}\right)^{M+1} - 1}{\left(\frac{(1-s)L_T}{K^{II} V_F^{II}}\right)^{M+1} - 1} + \\ l_T s \frac{\left(\frac{K^I V_F^I}{sL_T}\right)^{N+1} - \left(\frac{K^I V_F^I}{sL_T}\right)}{\left(\frac{K^I V_F^I}{sL_T}\right)^{N+1} - 1} + \\ l_T (1-s) \frac{\left(\frac{K^{II} V_F^{II}}{(1-s)L_T}\right)^{M+1} - \left(\frac{K^{II} V_F^{II}}{(1-s)L_T}\right)}{\left(\frac{K^{II} V_F^{II}}{(1-s)L_T}\right)^{M+1} - 1} \quad (17)$$

If eq 17 is evaluated to yield a fully expanded numerator over a fully expanded common denominator, the resulting numerator is a polynomial equation in the split fraction, s . As an example of the nature of the resulting polynomial equation, assume that $N = M = 1$. Then from eq 17, we obtain

$$s^3[-\alpha\beta l_T + \alpha^2\beta v_T - \alpha^2 l_T] + \\ s^2[-\alpha\beta v_F^I + \alpha\beta l_T + 2\alpha\beta v_T - \alpha l_T - \beta l_T - \alpha^2\beta v_T + \\ \alpha^2 v_F^{II} + \alpha^2 l_T - \alpha^2 v_T] + s[\alpha\beta v_F^I - 2\alpha\beta v_T + \alpha v_F^I + \\ 2\alpha v_F^{II} + 2\alpha l_T - 2\alpha v_T - \beta v_F^I + \beta l_T + \beta v_T] + \\ [v_F^I + v_F^{II} + l_T - v_T + \beta v_F^I - \beta v_T] = 0 \quad (18)$$

where

$$\alpha = L_T/K^I V_F^I \quad \text{and} \quad \beta = L_T/K^{II} V_F^{II}$$

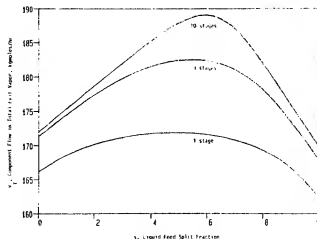


Figure 14. Multiple solutions for parallel cascades.

Suppose that we specify $v_F^I = 100$, $v_F^{II} = 50$, $V_F^I = 50v_T$, $V_F^{II} = 300$, $L_T = 200$, $L_T = 1000$, and $K^I = K^{II} = 1.2$. Solving eq 18 for v_T as a function of s gives the result shown in Figure 14. As seen, for v_T in the range of 166.2 to approximately 172, two solutions exist. For example, for $v_T = 170$, eq 18 reduces to

$$s^3 - 0.34545s^2 - 0.42545s + 0.0850909 = 0 \quad (19)$$

which, by Descartes rule of signs, predicts two real positive roots for s . The existence of two solutions persists for larger numbers of stages. Results for $N = M = 3$ and $N = M = 10$ are included in Figure 14. It is also clear from Figure 14 that a specification of s , rather than v_T , leads to a unique root for v_T .

Conclusions

The work of Wayburn and Seader (1984) has been extended and expanded to determine all multiple solutions for a Petlyuk separation system over a range of reflux ratios, when the purities of the three product streams and the bottoms total flow rate are specified. Four steady-state solutions were identified for that system, which involves two pairs of interlinks. For each of two other interlinked systems involving a single pair of interlinking streams, only two different steady-state solutions were found.

The degrees-of-freedom analysis showed that multiple solutions may occur when two sections of the system must share a specification in order to satisfy local degrees of freedom. The actual number of solutions, however, depends also on the configuration of the system and on the values of the specifications. For instance, the Petlyuk system studied here may have four, three, two, one or no physically meaningful solutions, depending on the value of the reflux ratio.

A mathematical analysis based on the simplified group method of Kremser showed that when two parallel sections of a separation system share a specification in order to satisfy local degrees of freedom, a maximum of two physically acceptable solutions for the system may occur. If more than two pairs of sections sharing specifications exist in the system, the possible number of solutions increases accordingly. This is the case for the Petlyuk system in which two pairs of sections share specifications and the

maximum number of real positive steady-state solutions is four.

This study establishes a basis to explore other types of interlinked systems, or even entire processes that contain sections sharing specifications and, therefore, may involve multiple solutions as well.

Acknowledgment

Mr. Wen-Jing Lin provided assistance in the approximate mathematical analysis. The research was partially supported by the Phillips Petroleum Foundation, Inc., and by Conacyt, Mexico.

Nomenclature

- A = absorption factor, L/KV
- B = total bottoms flow rate, kg-mol/h
- C = total number of components
- D = total distillate flow rate, kg-mol/h
- F = total feed flow rate, kg-mol/h; function
- H = homotopy
- L = liquid flow rate, kg-mol/h
- L' = liquid flow rate, kg-mol/h
- l = component liquid flow rate, kg-mol/h
- M, N = numbers of theoretical stages
- P = pressure, kPa; total flow rate of middle product, kg-mol/h
- R = reflux ratio
- S = stripping factor, KV/L
- s = split fraction
- T = temperature, K
- t = homotopy parameter
- V = vapor flow rate, kg-mol/h
- V' = vapor flow rate, kg-mol/h
- v = component vapor flow rate, kg-mol/h
- x = liquid mole fraction; variable
- y = vapor mole fraction

Greek Symbols

- $\alpha = L_T/K^I V_F^I$
- $\beta = L_T/K^{II} V_F^{II}$
- ϕ = recovery function

Subscripts

- A = absorption
- F = feed
- S = stripping
- T = total

Superscripts

- I, II = column designation

Registry No. Benzene, 71-43-2; toluene, 108-88-3; o-xylene, 96-47-6.

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Received for review June 16, 1986

Revised manuscript received July 3, 1986

Accepted July 28, 1986